

Specific Expectations

In this chapter, you will learn how to . . .

- C1.1 **assess** the benefits to society of technologies that are based on the principles of atomic and molecular structures (3.3)
- C2.1 **use** appropriate terminology related to structure and properties of matter (3.1, 3.2, 3.3)
- C2.2 **use** the Pauli exclusion principle, Hund's rule, and the aufbau principle to **write** electron configurations (3.3)
- C3.1 **explain** how experimental observations and inferences made by Ernest Rutherford and Niels Bohr contributed to the development of the planetary model of the hydrogen atom (3.1)
- C3.2 **describe** the electron configurations of a variety of elements in the periodic table, using the concept of energy levels in shells and subshells, as well as the Pauli exclusion principle, Hund's rule, and the aufbau principle (3.2, 3.3)
- B3.3 **identify** the characteristic properties of elements in each of the *s*, *p*, and *d* blocks of the periodic table, and **explain** the relationship between the position of an element in the periodic table, its properties, and its electron configuration (3.2, 3.3)

Fossils of birds and their ancestors sometimes capture the shapes and textures of plumage. However, until recently, the colours of long-extinct birds were a matter for speculation, inference, and sometimes even flights of fancy. In 2011, researchers developed a technique for analyzing fossil feathers, using a particle accelerator called a synchrotron to produce a very intense, narrowly focussed X-ray beam. Specific wavelengths of X rays are absorbed by atoms of different elements. The researchers were able to identify copper atoms that, in conjunction with a pigment called eumelanin, are found in dark-coloured feathers. They compared their data from 120 million year old fossils of birds with feathers of modern birds and confirmed their results. The data allowed these researchers to determine colour patterns on the feathers of the oldest-known beaked bird, *Confuciusornis sanctus*, shown here in this artist's conception.



Flame Tests to Identify Elements

When a compound containing a metal is heated in a flame, a distinctive colour is emitted that corresponds to that particular metal. In this activity, you will observe flame tests on solutions of metal-containing compounds and use your observations to identify the metal in an unknown compound.

Safety Precautions



- Wear safety eyewear throughout this activity.
- Tie back loose hair and clothing.
- Use EXTREME CAUTION when near an open flame.

Materials

- Bunsen burner
- heat-resistant pad
- wooden splint soaked in water
- labelled dropper bottles containing aqueous solutions of lithium hydroxide, sodium chloride, potassium chloride, calcium chloride, and strontium chloride
- labelled dropper bottle containing an unknown solution

Procedure

1. **Note:** Your teacher will demonstrate the flame tests with solutions of each of the known metallic compounds. Design a table to record your observations of the flame colour for each compound tested.
2. Obtain a sample of an unknown solution from your teacher.
3. Set up the Bunsen burner on the heat-resistant pad. Light the burner, and adjust the air supply to produce a hot flame with a blue cone.
4. Wet one end of a water-soaked wooden splint with a few drops of the unknown solution. Hold the wooden splint at the edge of the Bunsen burner flame. (You may need to hold the splint in the flame for up to 30 s until the solution vaporizes and mixes with the flame.)
5. Observe and record the colour of the flame.
6. Dispose of the used splint as instructed by your teacher.

Questions

1. Four of the known compounds tested contain chlorine, and one compound contains the hydroxide ion. Does this complicate the interpretation of the data? Explain your reasoning.
2. What is the identity of the unknown solution? Explain how you know.
3. Explain the importance of purity of the sample being tested. In what ways could contaminants affect the accuracy of the flame test?

Key Terms

nuclear model
electromagnetic radiation
frequency
photon
emission spectrum
line spectrum
quantum

The scientific concept of the atom as a physical component or constituent of matter is barely 200 years old. In that brief time, scientists' model of the atom has undergone remarkable changes—from a lawn-bowling ball, to a plum pudding, to a planetary system, to a quasi-particulate entity surrounded by even tinier fundamental entities that are neither particles nor waves and that can be described only by using mathematical equations. This last model, called the quantum mechanical model of the atom, will be introduced later, in Section 3.2.

To help you understand how and why the quantum mechanical model was developed, Section 3.1 will focus on the atomic models developed by two chemists, Ernest Rutherford and Niels Bohr, whose experiments, ideas, and insights were central to the conception of the quantum mechanical model. To set the stage, two earlier models, those of John Dalton and J.J. Thomson, are briefly reviewed first.

Reviewing the Atomic Models of Dalton and Thomson

John Dalton (1766–1844) was a schoolteacher and scientist whose atomic theory, published in 1808, marked the beginning of a new way to describe, explain, and visualize the nature of matter. Dalton's interest in the gases that make up Earth's atmosphere led him to investigate the composition and properties of substances such as carbon dioxide, water vapour, and nitrogen monoxide. In explaining some of his experimental results, Dalton compared the particles that make up matter to small, hard spheres, to which he gave the name atoms.

Figure 3.1 shows models of these spheres.

Figure 3.1 Dalton was an avid lawn-bowler, so it is not surprising that he visualized atoms in the form of tiny solid spheres. He likely also was influenced by Sir Isaac Newton's description of matter as being formed from "solid, massy, hard, impenetrable, movable particles" (from *Opticks*).



According to Dalton's model, the atom was indestructible and indivisible. However, a series of investigations beginning in the 1850s and extending into the early 1900s demonstrated that atoms are not indivisible—that they are made up of even smaller components. These investigations led to the discovery of electrons, protons, and neutrons, and contributed to scientists' understanding of atomic structure.

The first of these smaller components to be discovered was the electron, and the person who discovered it was Joseph John (J.J.) Thomson (1856–1940). Thomson, a physicist, was especially interested in studying electric currents in gas discharge tubes, which are glass tubes from which most of the air has been removed. The glass tubes, called cathode ray tubes, are fitted with metal electrodes that are sealed in place and connected to an external source of electrical energy. An example of a cathode ray tube is shown in **Figure 3.2**.

When the power is turned on, a “ray” emanates from the negative electrode (cathode) and travels to the positive electrode (anode). Because the nature of the “ray” was not known, they were simply called cathode rays. Thomson and other scientists who worked with cathode ray tubes observed that the results of their many experiments did not depend on the material from which the cathode was made. Cathode rays appeared to be a component even more fundamental than atoms and common to all matter. As well, when a magnet was placed near the tube, as demonstrated in **Figure 3.2**, the path of the ray curved in the direction that negative charges should move. Thomson determined in 1897 that the cathode rays were streams of negatively charged particles—electrons.

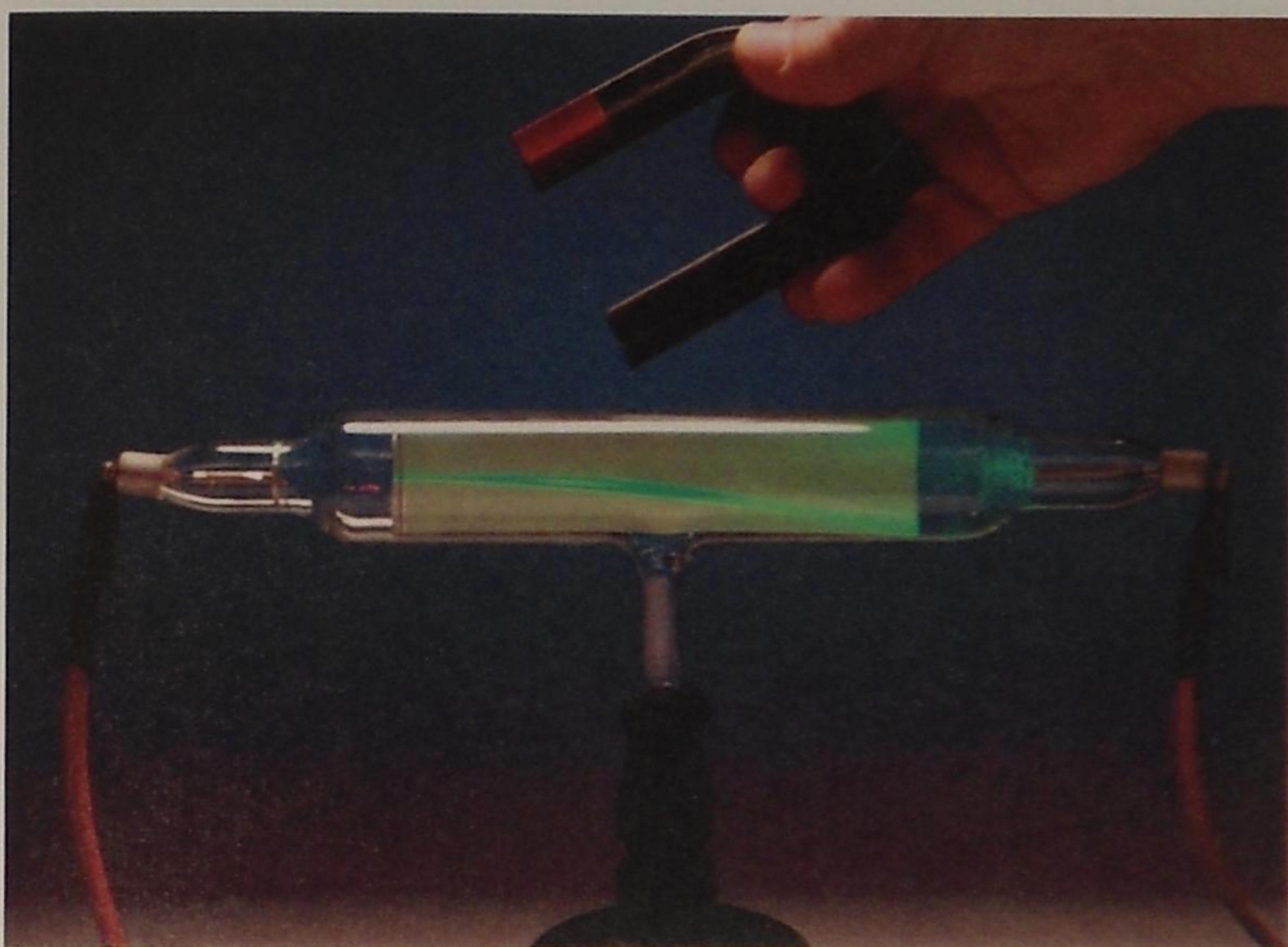


Figure 3.2 Cathode rays are invisible, but when they collide with the few remaining gas molecules in the tube, they excite atoms in the gas molecules. These excited atoms emit visible light, making the path of the cathode rays visible.

Based on his studies, Thomson proposed a model of the structure of the atom based on a plum pudding, a popular cake-like dessert that was common in England. (A plum pudding was originally made with dried plums and later evolved to use currants, raisins, or any other dried fruit.) This plum pudding model, shown in **Figure 3.3**, portrayed the atom as a positively charged, spherical mass in which negatively charged electrons (the “plums”) were embedded and held by electrostatic forces.

Thomson presented his atomic model during a series of lectures in 1903 and later published his ideas in 1904. For the scientific community, however, this model was short-lived. By 1911, a more complete and accurate model of the atom was proposed by one of Thomson’s students, a chemist and physicist named Ernest Rutherford.

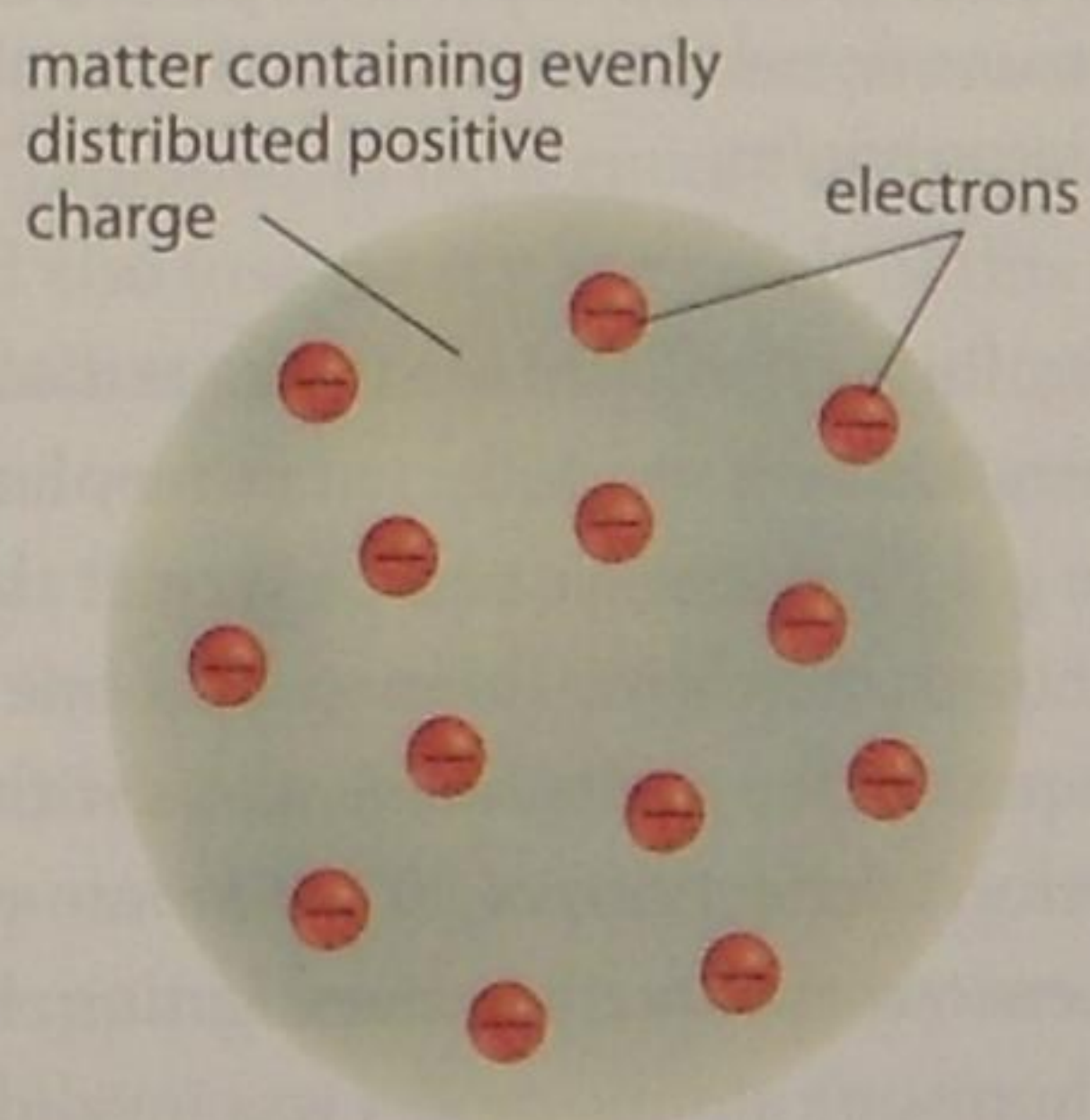


Figure 3.3 The Thomson model of the atom. **Analyze** Originally referred to as the “plum pudding model,” Thomson’s model is also called a “raisin bun model” or a “blueberry muffin model.” How do comparisons like these help in communicating scientific ideas?

Rutherford's Experiments with Alpha Particles

At the end of the 19th century, French physicists Henri Becquerel and Marie and Pierre Curie discovered that certain elements are radioactive—they naturally emit positively charged particles (alpha particles), negatively charged particles (beta particles), and electromagnetic energy (gamma radiation). Between 1898 and 1907, New Zealand-born British chemist Ernest Rutherford (1871–1937) began intensive studies of the chemistry of radioactive elements while working at Montreal's McGill University. His efforts would lead to a Nobel Prize in chemistry in 1908.

In 1909, two of Rutherford's students reported observations that cast doubts on Thomson's atomic model. As part of ongoing investigations into the nature and properties of radioactive emissions, the students aimed alpha (α) particles at extremely thin sheets of gold foil. The gold foil was surrounded by a zinc sulfide-coated screen that produced a flash of light whenever it was struck by an alpha particle. By noting where the flashes occurred, the researchers could determine if and when the atoms in the gold foil deflected the alpha particles.

Based on Thomson's atomic model, the researchers expected to observe only minor deflections of the alpha particles. As shown in **Figure 3.4**, they expected the paths of the large, fast-moving alpha particles to be altered only slightly by a nearby encounter or collision with an electron. With Thomson's model of the atom in mind, Rutherford also believed that, because the positive charge within the gold atoms was uniformly distributed, it would not affect the paths of the alpha particles.

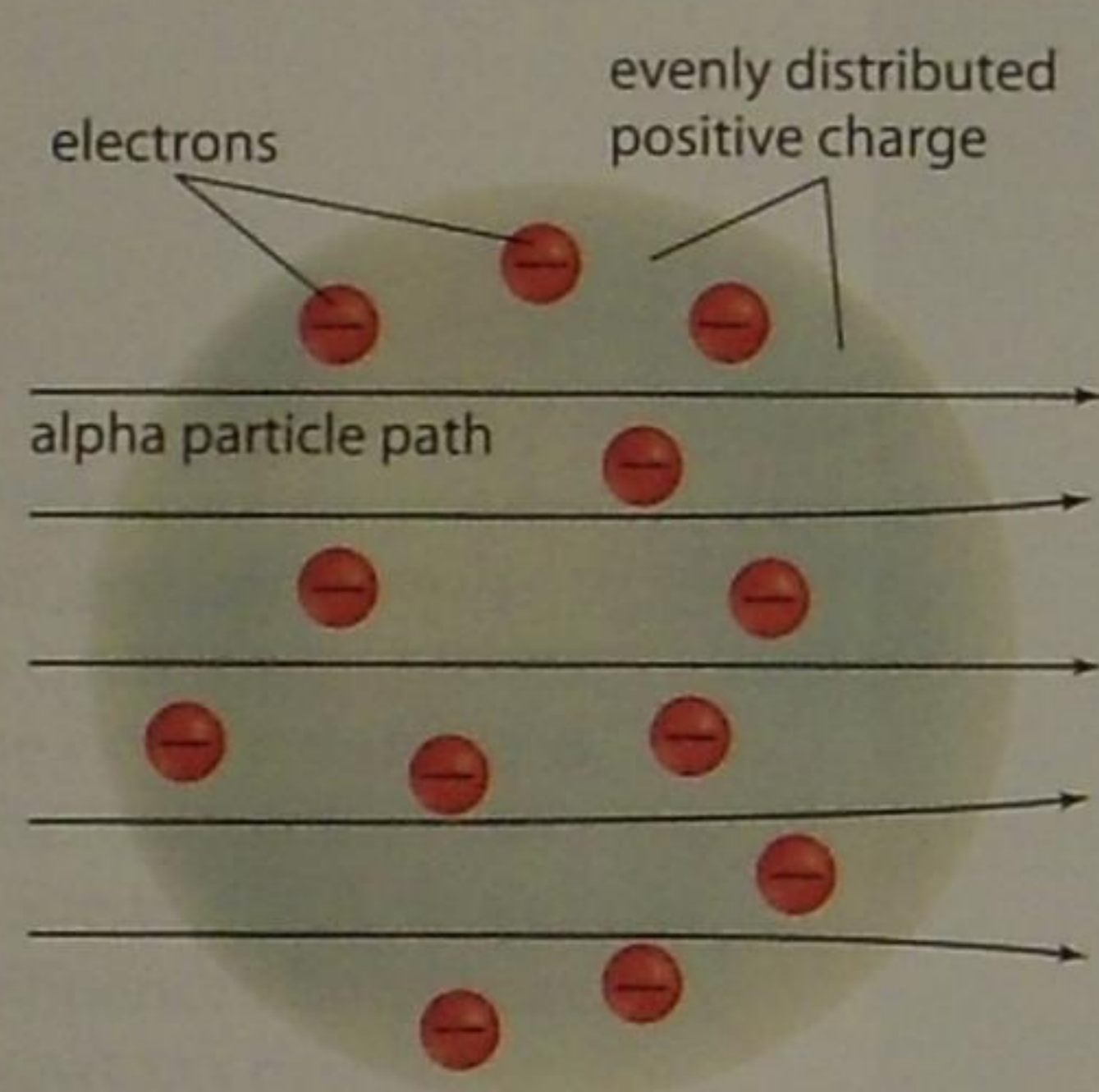


Figure 3.4 Rutherford and his students expected most of the large, highly energetic alpha particles to pass straight through the gold foil atoms. They also expected some alpha particles to be slightly deflected by the electrons in the gold foil atoms.

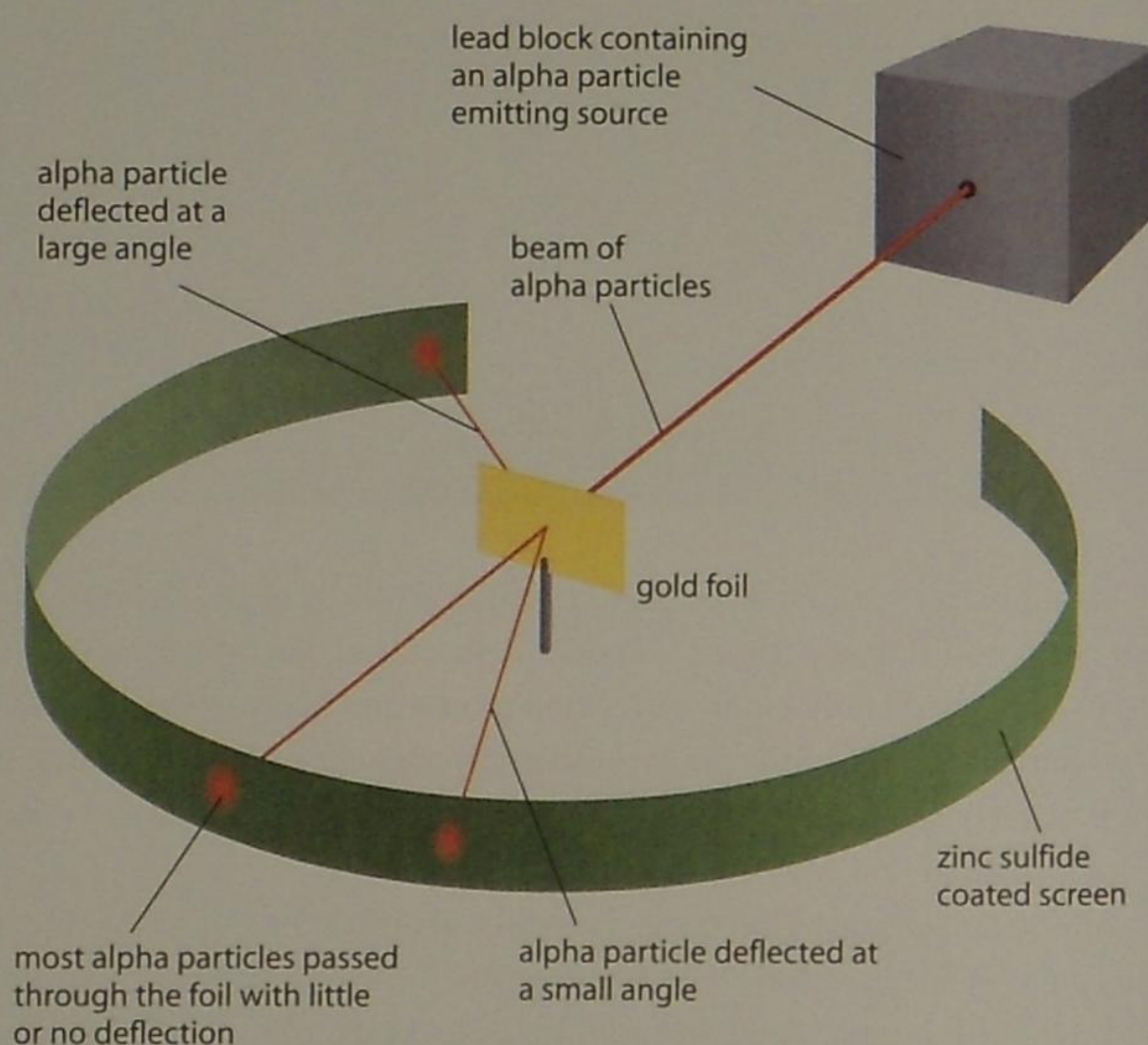


Figure 3.5 Rutherford's experiment was designed to measure the scattering of alpha particles when directed at a thin gold foil. Most of the alpha particles passed directly through the gold foil with little or no deflection. However, some were scattered at small angles, and a few alpha particles were deflected at very large angles.

After several days of testing, Rutherford and his students discovered that some of the alpha particles—about 1 in every 8000—were deflected at very large angles. About 1 in 20 000 were deflected from the gold foil at angles much greater than 90° , as shown in **Figure 3.5**. These observations were inconsistent with Thomson's atomic model. The researchers expected the alpha particles to pass through the metal atoms with deflections averaging $\frac{1}{200}$ of a degree, at most. Therefore, deflections of 90° and more strained the credibility of Thomson's model. Rutherford encouraged further investigation. Either their observations and the data were flawed, or Thomson's atomic model was invalid.

Rutherford's Atomic Model

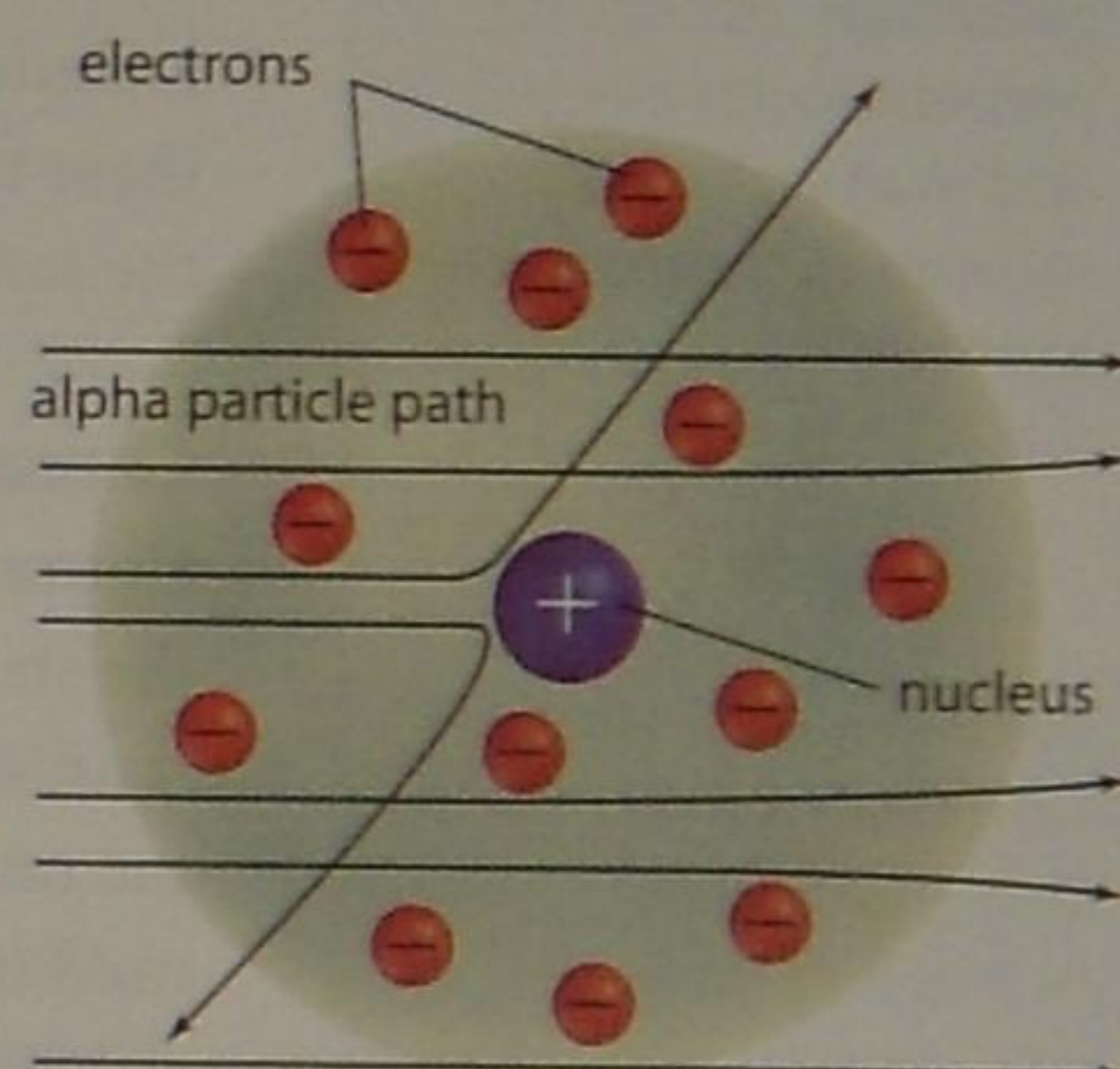
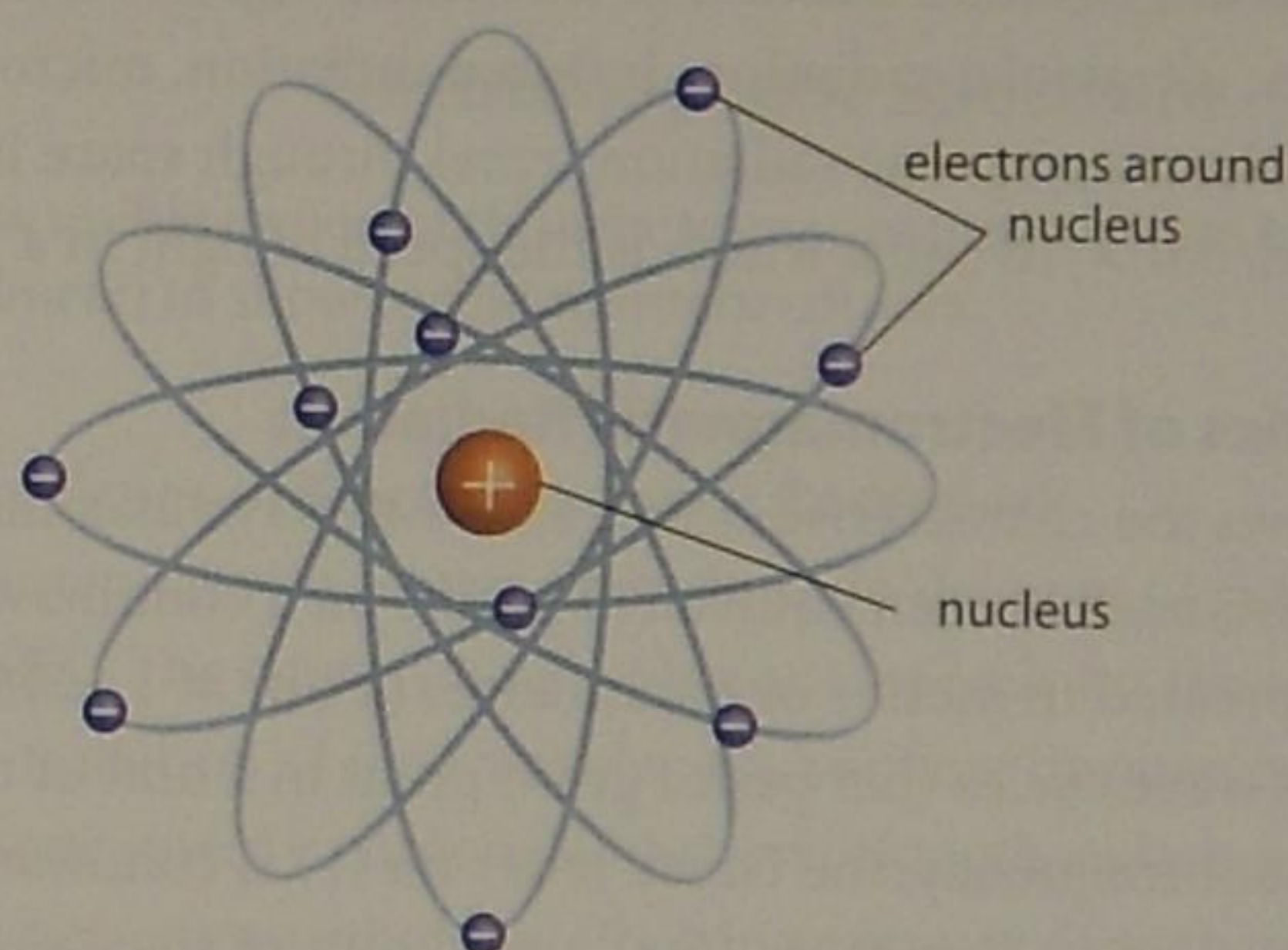
In 1911, Rutherford published the results of the gold foil experiments undertaken by him and his students. Based on their experimental findings, Rutherford proposed that the observed deflections were caused by encounters between alpha particles and an intense electric field at the centre of the atom. Since these results were inconsistent with Thomson's model of the atom, Rutherford developed a new atomic model.

Given the properties of the alpha particles and electrons, and the frequency and the angles of the deflections that were observed, Rutherford calculated that all of the positive charge and most of the atom's mass were confined to a very small region at the centre of the atom, which he called the nucleus. Rutherford's atomic model, shown in **Figure 3.6**, depicts electrons in motion around an atomic nucleus, so chemists often call this the **nuclear model** of the atom. It is sometimes also referred to as a *planetary model*, because the electrons resemble planets in motion around a central body.

Figure 3.7 shows how Rutherford's nuclear model of the atom explained the results of the gold foil experiments. The repulsive force that occurred between the positive nucleus and the positive alpha particles caused the deflection of the alpha particles. When alpha particles *closely* approached the nucleus, they were deflected at small angles. However, when alpha particles *directly* approached the nucleus, they were deflected at very large angles. The nuclear model also explains the neutral nature of matter—that is, the positive charge of the nucleus balances the negative charge of the electrons. Despite these findings, however, Rutherford's model still could not account for all of the atom's mass. Another 20 years would pass before this discrepancy was finally explained by James Chadwick's discovery of the neutron.

nuclear model a model of the atom in which electrons move around an extremely small, positively charged nucleus; also called a *planetary model*

Figure 3.6 The atomic model that Rutherford proposed in 1911 is known as the nuclear, or planetary, model of the atom.



The Limitations of Rutherford's Atomic Model

Rutherford's atomic model answered some of the questions arising from Thomson's atomic model, but it also raised others. First, an atomic nucleus composed entirely of positive charges should break apart as a result of electrostatic forces of repulsion. Second, until the discovery of the neutron 20 years later, Rutherford's nuclear atom could not adequately explain the total mass of an atom.

There was a more significant problem, however. According to the scientific laws and understandings of physics before the turn of the 20th century, an electron in motion around a central body *must* continuously emit radiation. Therefore, one would expect to observe a continuous spectrum, or "rainbow," of light energy as the electron gives off radiation. Because the electron should also lose energy as a result of this radiation, the radius of its orbit should continuously decrease in size until it spirals into the nucleus, obliterating the atom entirely. Since this does not occur, either the Rutherford model was incorrect or scientists' understanding was flawed—perhaps even both.

Science, as understood and explained by the physicists of the late 1800s, could not explain why Rutherford's model corresponded to a stable atom. The solution to this problem marked a turning point in the history of chemistry and physics, because it required scientists to think about energy and matter in a startlingly new way.

Figure 3.7 Rutherford's nuclear model explained the unexpected interactions of alpha particles with the gold foil. The strong repulsive force between the positively charged nucleus and the positively charged alpha particles caused their deflections.

Learning Check

1. What evidence invalidated Dalton's atomic theory that atoms are indivisible?
2. If Thomson's model of the atom had been valid, what would Rutherford and his team have observed in the gold foil experiment, and why?
3. State one way the discovery of radioactive elements furthered the development of atomic theory.
4. Draw two labelled diagrams with captions to summarize Thomson's and Rutherford's atomic models.
5. Dalton enjoyed lawn-bowling, and plum pudding was a popular dessert in England long before Thomson was even born. What role do you think that personal interests and cultural history play in the kinds of models that scientists use to communicate their ideas? Use another example to explain your answer.
6. Explain why Rutherford and his students expected to observe only minor deflections of alpha particles, based on Thomson's model.

Rethinking Atomic Structure Based on the Nature of Energy

By the early 1900s, scientists were starting to gain a better understanding of chemical behaviour. For instance, they had long known that atoms could emit light when stimulated by an electric current. In fact, chemists knew that they could identify elements by the set of specific wavelengths of light that atoms of each element emit when stimulated. However, they had no idea how or why this occurred. To learn how chemists used this information, it will be necessary to review some key ideas about the nature of light.

Light is a form of energy called **electromagnetic radiation**. The light that you see—visible light—is only a small fraction of the wide range of electromagnetic radiation, which includes X rays, ultraviolet radiation, infrared radiation, microwaves, and radio waves. All these types of electromagnetic radiation travel through space in the form of waves and at the same speed, 3.0×10^8 m/s, which is the speed of light in a vacuum.

electromagnetic radiation oscillating, perpendicular electric and magnetic fields moving through space as waves

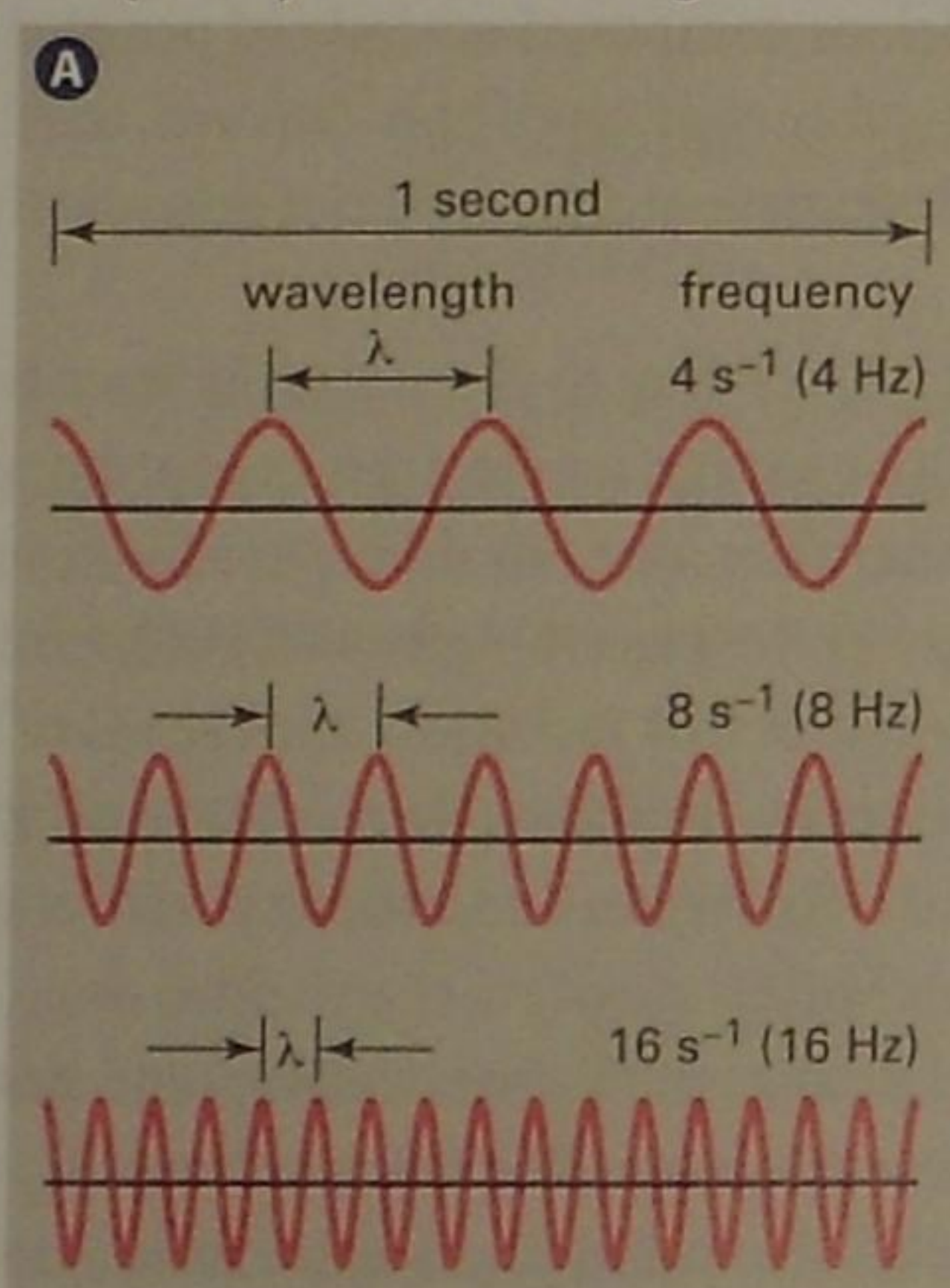
frequency the number of complete wave cycles that pass a given point in a unit of time

Characteristics of Electromagnetic Radiation

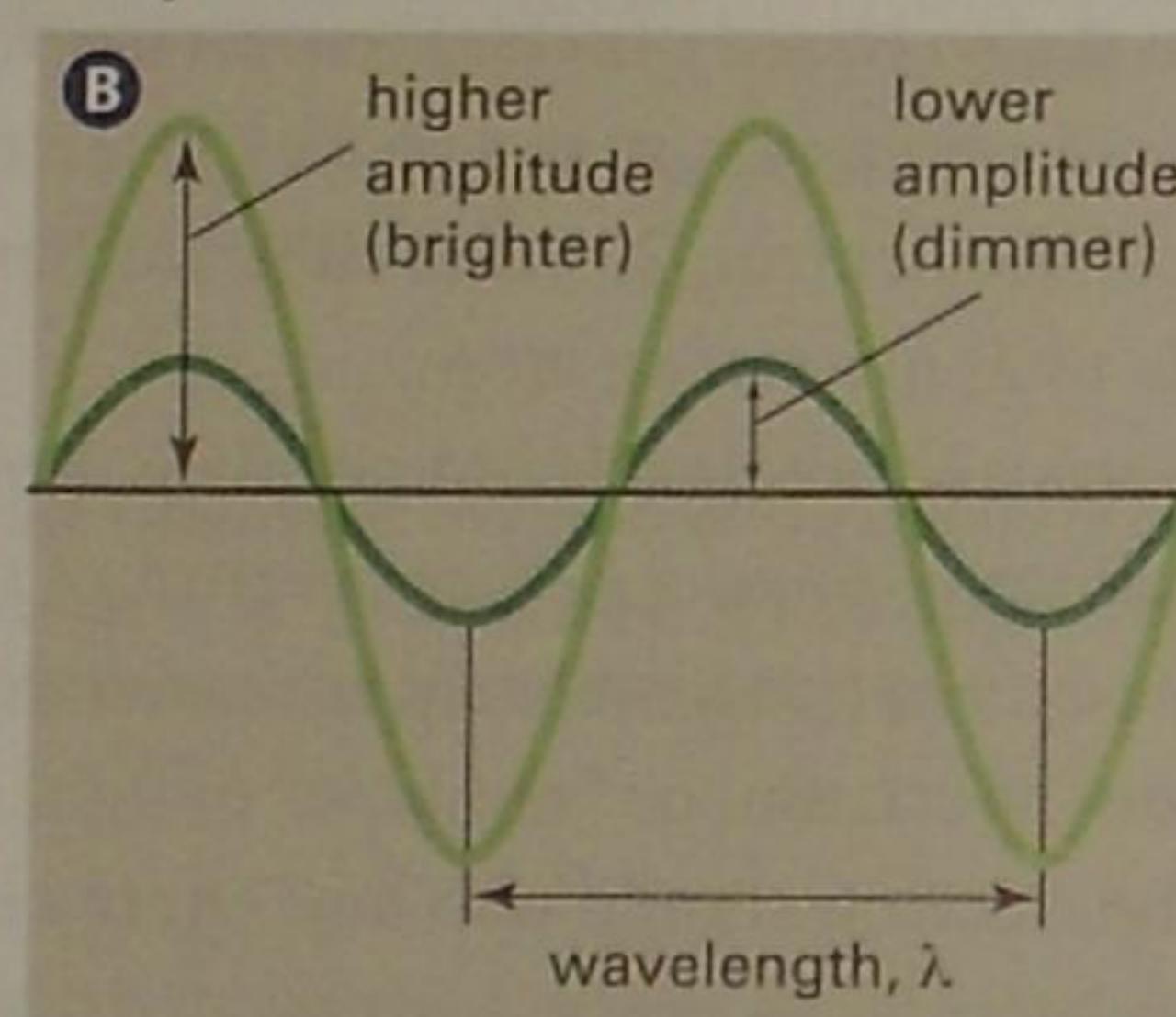
Figure 3.8 shows the characteristics that all waves have in common. **Wavelength** (λ) is the shortest distance between equivalent points on a continuous wave. Wavelength is most often expressed in metres or nanometres ($1 \text{ nm} = 1 \times 10^{-9} \text{ m}$). **Frequency** (ν) is the number of wave cycles that pass a given point in a unit of time. Although f is often used to represent frequency, the Greek letter nu (ν) is commonly used when describing electromagnetic waves. One hertz (Hz), the SI unit of frequency, represents one cycle per second (s^{-1}).

Figure 3.8 (A) Three waves with different wavelengths (λ) and frequencies (ν) are shown. Note that as the wavelength decreases, the frequency increases. **(B)** The amplitude of a wave represents its intensity. For visible light, this is perceived as brightness of the light. Here, the two waves have the same wavelength but different amplitudes; therefore, each wave has a different brightness.

Frequency and Wavelength



Amplitude of a Wave



A labelled diagram of the electromagnetic spectrum is shown in **Figure 3.9**. Notice that as wavelength decreases, frequency increases. In other words, wavelength and frequency are inversely proportional.

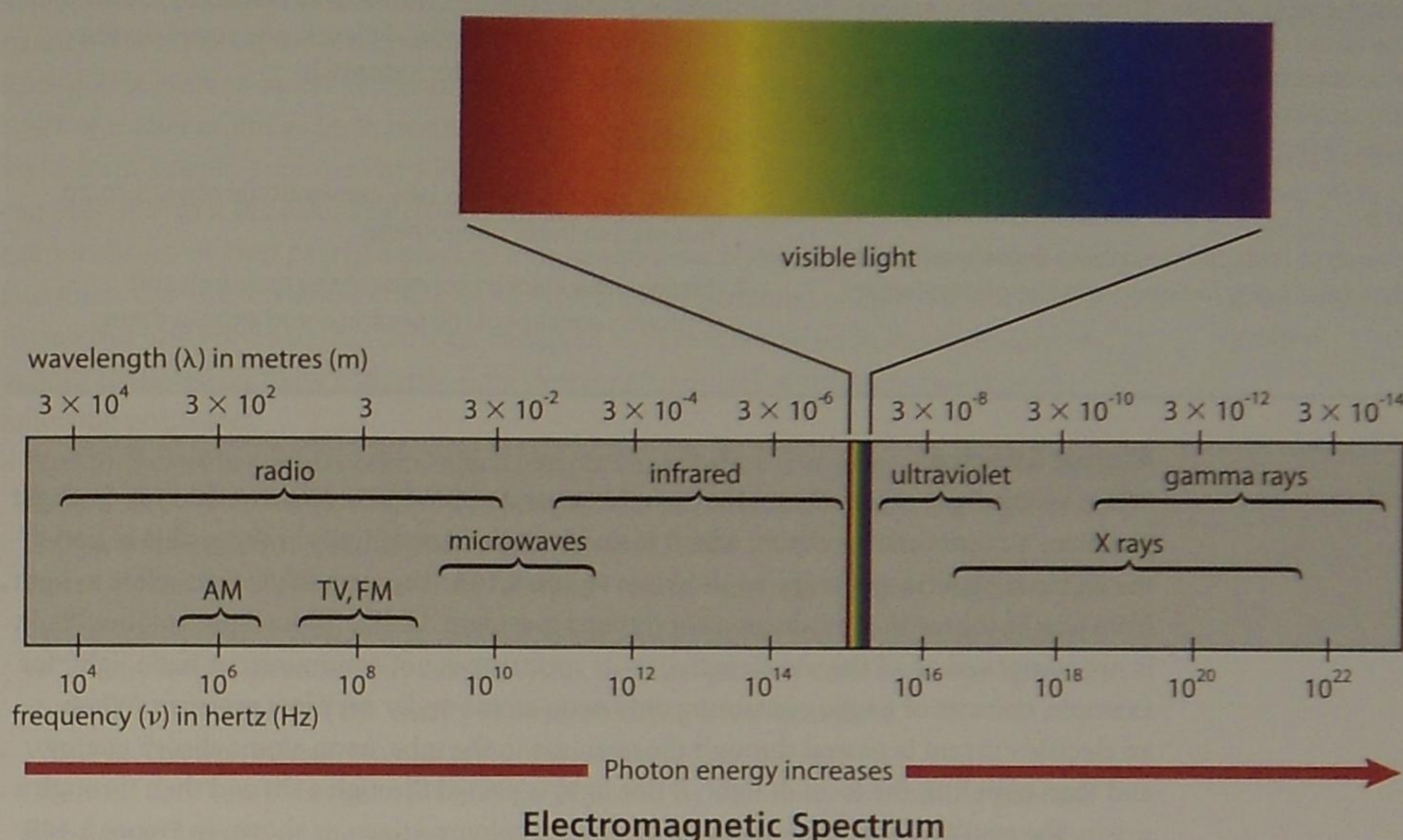


Figure 3.9 The relatively narrow visible region of this electromagnetic spectrum has been expanded (and the scale made linear) to show the component colours.

The Energy of Light and other Types of Electromagnetic Radiation

When electromagnetic waves interact with matter, they do so in discrete packets, or quanta, of energy called **photons**. The energy, E , of a photon depends on the wavelength or frequency. Electromagnetic radiation of long wavelength and low frequency, such as radio waves, is composed of lower-energy photons. Short-wavelength radiation with high frequencies is composed of higher-energy photons. Photon energy is directly proportional to frequency and inversely proportional to wavelength.

Mathematical relationships can be used to calculate the wavelength (λ), frequency (ν), and photon energy of electromagnetic radiation. The product of frequency and wavelength is a constant, c , which is the speed of light in a vacuum: $\nu\lambda = c$. This equation shows the inverse relationship between wavelength and frequency. Since the speed of light in a vacuum, c , is a constant, when frequency is large, wavelength must be small; when wavelength is large, frequency must be small. If the value of either wavelength or frequency is known, you can calculate the unknown value by rearranging the equation:

$$\nu = \frac{c}{\lambda} \text{ or } \lambda = \frac{c}{\nu}$$

The mathematical relationships between photon energy and frequency and between photon energy and wavelength are described by the following equations, where h is a constant with a value of 6.626×10^{-34} J·s:

$$E_{\text{photon}} = h\nu \quad E_{\text{photon}} = \frac{hc}{\lambda}$$

(The constant, h , is called Planck's constant. You can investigate the significance of this constant and the scientist, Max Planck, who discovered it, in Activity 3.1.)

photon a packet, or quantum, of electromagnetic energy

The concepts of the quantum and the photon developed mostly from the work of Max Planck and Albert Einstein as they attempted to understand and explain two phenomena: blackbody radiation and the photoelectric effect. In this activity, you will investigate these phenomena and the work of these two scientists.

Procedure

1. Do research to help you describe—verbally as well as visually—blackbody radiation and the photoelectric effect.

2. In the course of your research, refer to Planck, Einstein, and any other scientists whose work helped to inform their thinking. (In the case of Planck, one such scientist was Gustav Kirchhoff, for instance.)

Questions

1. Summarize the reasons why conventional physics could not explain these phenomena.
2. Explain how Planck's concept of the quantum and Einstein's concept of the photon could explain them.

Atomic Spectra

When visible light passes through a prism, it separates into its component colours. Sunlight produces a *continuous spectrum*, which includes all the wavelengths in the visible region of the electromagnetic spectrum, as shown in **Figure 3.10A**. The term *white light* refers to light from a light source that produces a continuous spectrum. Unlike white light, coloured light is not composed of all the wavelengths, so its spectrum is not continuous. A neon light, for example, consists of a tube containing only neon atoms under very low pressure. When an electric current is passed through the neon gas in the tube, neon atoms absorb energy and then emit it in the form of light. If this light is passed through a slit and then through a prism, the resulting spectrum has a set of distinct coloured lines, as shown in **Figure 3.10B**. Each coloured line represents a single wavelength of light, and the pattern of these lines is called an **emission spectrum** or a **line spectrum**.

When atoms of an element are excited (absorb energy), the energy can be emitted as light energy. The light that atoms of a given element produce in this way contains only specific colours, as shown by its line spectrum. The line spectrum for each element is unique, so it can be used to identify the element. You will see in the following paragraphs how a Danish chemist named Niels Bohr, who worked briefly in the laboratories of both J.J. Thomson and Ernest Rutherford, related the line spectrum for hydrogen to its atomic structure.

emission spectrum or line spectrum

a series of separate lines of different colours of light emitted by atoms of a specific element as they lose excitation energy

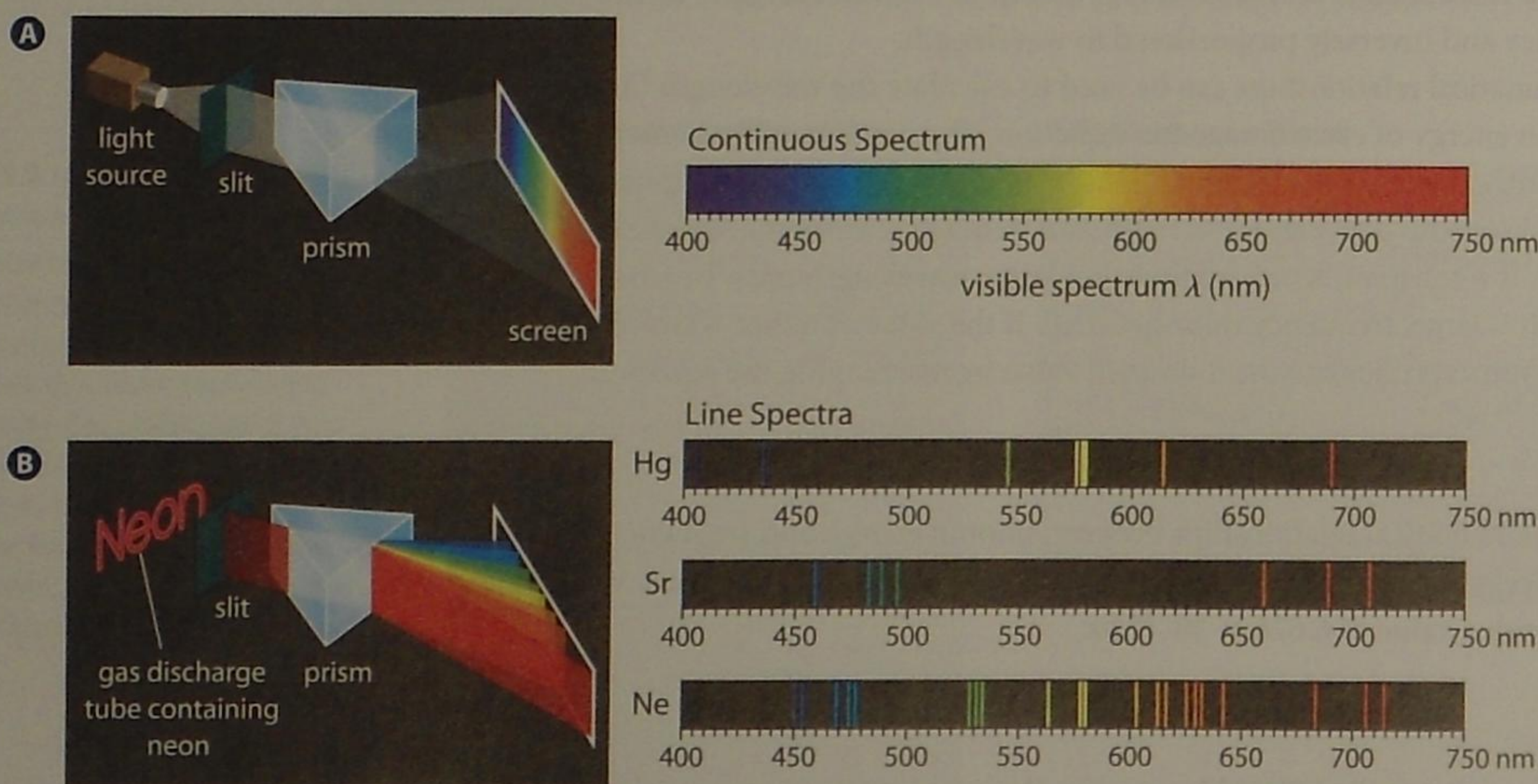


Figure 3.10 When white light passes through a prism, a continuous spectrum (**A**) is produced. The coloured light emitted by a substance, such as neon, produces a line spectrum (**B**) that is unique to that substance. Line spectra of various elements are shown here.

The Bohr Model of the Hydrogen Atom

One year after Rutherford published his nuclear model of the atom, Niels Bohr (1885–1962) came to work in his laboratory. Fascinated by this model, Bohr set out to explain the stability of the nuclear atom and why it appeared to contradict known laws of physics. He based his analysis on the recent work of Max Planck and Albert Einstein, as well as on the line spectra emitted by excited atoms. Bohr knew from a paper published by Planck in 1900 that hot matter emitted electromagnetic energy as discrete packets, or **quanta**, of energy. He knew from a paper published by Einstein in 1905 that when matter absorbs light energy, it can only absorb it in packets or photons in an “all or none” manner. In other words, matter cannot absorb or emit part of a photon or more than one photon in a single event. Bohr also knew that excited atoms emit specific wavelengths (photons) of light. He combined these ideas and reasoned that the total energy of each electron in an atom might also be quantized. Based on these concepts, Bohr developed a model of the atom based on the following postulates.

- Electrons exist in circular orbits, much like planetary orbits. The central force that holds them in orbit is the electrostatic force between the positive nucleus and the negative charge on the electrons, rather than a gravitational force.
- Electrons can exist only in a series of “allowed” orbits. Much like planets, electrons have different amounts of total energy in each orbit. Thus, these orbits can also be described as “energy levels.” Because only certain orbits are allowed, only certain energy levels are allowed. This means that the energy of electrons in atoms is quantized.
- While an electron remains in one orbit, it does not radiate energy.
- Electrons can “jump” between orbits (energy levels) by absorbing or emitting photons carrying an amount of energy that is equal to the difference in the energy levels of the electrons.

By using the basic laws of physics and Planck’s concepts, Bohr was able to calculate the energy and radii of the allowed orbits for the hydrogen atom. In Bohr’s atomic model, the orbits are numbered with $n = 1$ as the orbit nearest the nucleus. Bohr’s calculated radius of this orbit is $5.291\,77 \times 10^{-11}$ m, which is now called the Bohr radius. Because that orbit has the lowest possible energy, it is called the *ground state* of the atom. Energy is required to move the electron farther from the nucleus due to the attractive force of the nucleus. A model of the Bohr atom, with six of its orbits, is shown in **Figure 3.11**. The radii of the orbits are not drawn to scale; the distance between the orbits gets larger with each orbit.

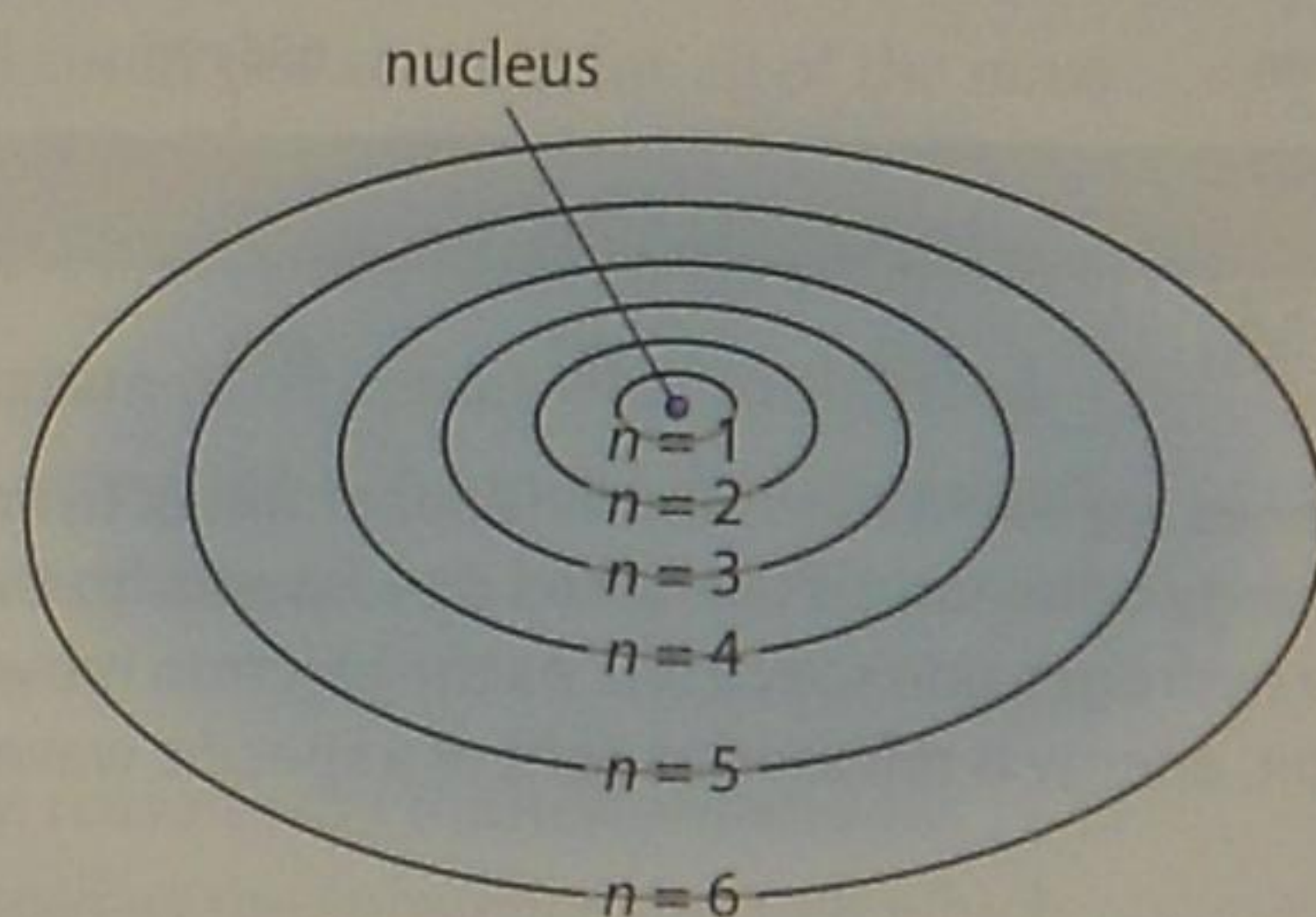


Figure 3.11 In the Bohr model of the hydrogen atom, the nucleus is at the centre of the atom, and the electron is located in one of the circular orbits, each with a specific energy and radius. Six orbits are shown here, but any number of orbits is possible.

According to Bohr’s model, an atom can absorb energy and become excited in one of two ways. The atom can collide with a highly energetic particle such as an electron in an electric current passing through a gas. Alternatively, the atom can absorb a photon that has an amount of energy equal to the difference between the energy of the orbit it occupies and the energy of a higher orbit. Excited atoms quickly return to their ground state by emitting photons of an energy equal to the difference between the energy of the orbit it occupies and a lower orbit.

Suggested Investigation

Inquiry Investigation 3-A,
Observing Spectra (Teacher
Demonstration)

quantum an indivisible packet of energy that must be absorbed or emitted in an “all or none” manner (plural, quanta)

Bohr's Atomic Model Explains the Line Spectrum of Hydrogen

With the aid of this new atomic model and the idea that the energy of the photons emitted by excited atoms had to be equal to the difference between energy levels, Bohr calculated the possible energies of the photons that could be emitted by excited hydrogen atoms. By using Planck's equation relating the energy of photons to their wavelength, $E = hc/\lambda$, Bohr calculated the value of the wavelengths of the electromagnetic radiation. The wavelengths that fell in the visible range of the electromagnetic spectrum were the transitions from energy levels $n = 6, 5, 4$, and 3 to energy level $n = 2$. When he compared them with the wavelengths of the experimentally observed spectrum, they were in complete agreement. As shown in **Figure 3.12**, the transition from energy level $n = 6$ to $n = 2$ produces a photon with a wavelength of 410 nm, which is in the range of violet light. The transition from $n = 5$ to $n = 2$ produces a photon with a wavelength of 434 nm, which is the range of indigo light. The last two transitions produce photons with wavelengths of 486 nm and 656 nm, which are blue light and red light, respectively.

During the same period that Bohr was doing his theoretical work, other scientists discovered spectra from hydrogen atom that were in the infrared and ultraviolet regions of the spectrum. The wavelengths of the photons in these spectra were also in agreement with Bohr's predictions. Such excellent agreement between Bohr's theoretical predictions and observed data provided strong support for Bohr's basic tenets.

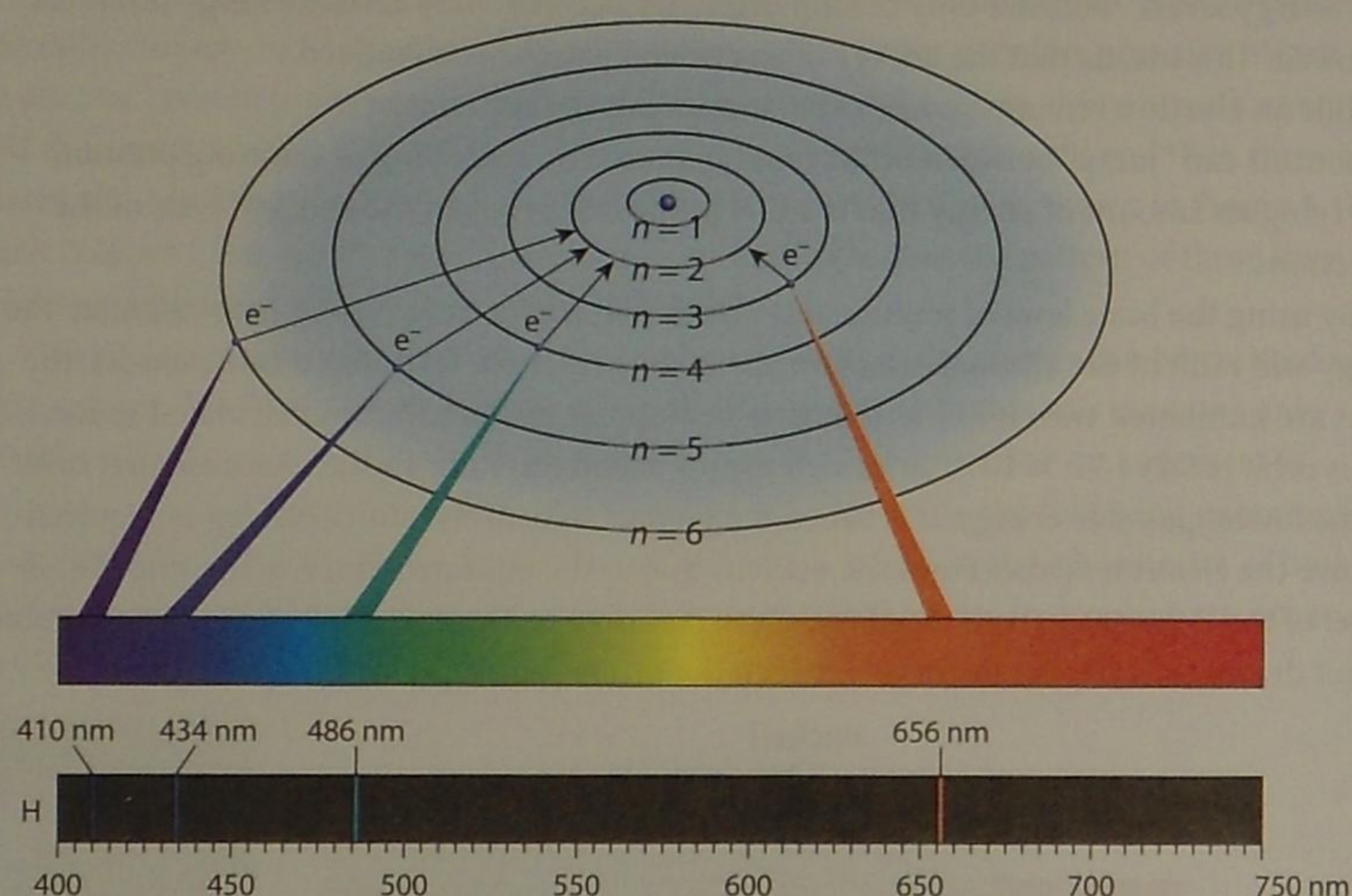


Figure 3.12 Four distinct lines appear in the visible line spectrum of hydrogen. In the Bohr model, the difference in energy between certain orbits corresponds to the photon energies of the lines that appear in the hydrogen line spectrum. As the electron moves from a higher-energy orbit to a lower-energy orbit, energy is released as light of a specific wavelength (and, therefore, of a specific colour).

The Limitations of Bohr's Atomic Model

Bohr's atomic model was successful in explaining the line spectrum of hydrogen. It also explained the line spectrum for single-electron ions such as He^+ and Li^{2+} . However, Bohr's model could not explain the line spectra for atoms that had two or more electrons, and so its value as a means for describing atomic structure was severely limited. Nevertheless, Bohr's ideas of quantized energy levels would prove to be of enormous benefit to other scientists working to solve the same fundamental problem of both describing and explaining atomic structure. In the next section, you will be introduced to the model that has resulted from their work: the quantum mechanical model of the atom.




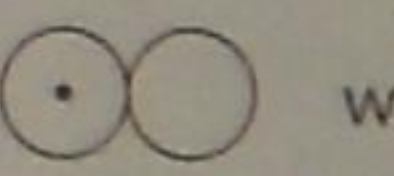


Section 3.1 Review

Section Summary

- Historically, the development of and modifications to the atomic model have been the result of experimental evidence leading to new ideas about the nature of matter and energy.
- Thomson's discovery of the electron disproved Dalton's model of the atom as a solid, indivisible sphere. Instead, Thomson proposed that the atom existed as a positively charged sphere, with enough negatively charged electrons embedded in it to balance the overall charge on the atom.
- Observations and inferences made by Rutherford led to a nuclear model of the hydrogen atom. This model is still the most commonly depicted, with negatively charged electrons orbiting around a central positively charged nucleus.
- Bohr's model of the atom refined the Rutherford model, incorporating the concept that, like light, electrons in atoms could have only certain amounts of energy and, therefore, could exist in only specific orbits around the nucleus. Each allowed orbit had a specific amount of energy and a specific radius.

Review Questions

- C** Your friend is conducting Internet research on the history of atomic theory and e-mails you to ask why Thomson's model of the atom is sometimes called the "plum pudding" model. Write a brief e-mail reply to explain, and use a similar analogy that might be more familiar to your friend.
- A** Dalton's atomic theory represented a huge step forward for a scientific understanding of the nature of matter. One of its successes was explaining observations about mass relationships in chemical reactions.
 - State and explain the law of conservation of mass in terms of Dalton's atomic model.
 - State one shortcoming of Dalton's model of the atom.
- K/U** Rutherford could not account for all of the mass in the nucleus when he first made observations. Describe the discovery that provided an explanation.
- C** Draw a diagram to represent what Rutherford and his colleagues expected to happen when they fired alpha particles through a gold foil, based on Thomson's model of the atom.
- A** Suggest one reason why Rutherford and his colleagues chose gold as the substance through which to fire alpha particles.
- C** Compare Rutherford's model and Thomson's model of the atom using a Venn diagram.
- K/U** What is the key difference between Rutherford's model and Bohr's model, and what shortcoming of Rutherford's model does this key difference address?
- A** Why are only the transitions from $n = 3, 4, 5$, and 6 to $n = 2$ shown in **Figure 3.12**?
- T/I** Arrange the following types of electromagnetic radiation from lowest energy to highest energy. For each type, state which has the highest and lowest frequency and the longest and shortest wavelength.
 - gamma ray, microwave, visible light
 - visible light, X ray, infrared light
 - ultraviolet ray, X ray, radio wave
- K/U** According to 19th century physics, what type of radiation should an atom based on Rutherford's model emit? What were excited atoms observed to emit?
- T/I** When an electron in a hydrogen atom absorbs a photon of blue light with a wavelength of 434 nm, it moves from one energy level to another.
 - What energy level did the electron occupy originally?
 - What energy level does the electron occupy after emitting the photon?
- A** Dalton invented symbols such as those shown below to represent atoms and molecules. Suggest a reason why his symbols could represent carbon dioxide accurately but not water or methane.

 hydrogen	 carbon dioxide
 carbon	 water
 oxygen	 methane
- K/U** How does the idea of quantized energy apply to Bohr's atomic model?
- C** A ladder and a ramp are one analogy for quantized vs. continuous theories of energy. Think of another analogy to compare the two theories and draw a diagram to represent it.

Key Terms

quantum mechanical
model of the atom
atomic orbital
quantum number
principal quantum
number, n
shell
orbital-shape quantum
number, l
sublevel
magnetic quantum
number, m_l
spin quantum number, m_s
Pauli exclusion principle

While a graduate student at the Sorbonne in Paris, France, Louis de Broglie was doing an in-depth study of the recently published concepts in the particle theory of light. This theory suggested that light interacts with matter as individual photons. De Broglie reasoned that, if light waves have some properties of particles, then particles might have some properties of waves. He used some of the concepts involving light waves and applied them to particles such as electrons. He determined that the wavelength for particles should be $\lambda = h/mv$, where h is Planck's constant, m is the mass of the particle, and v is the speed of the particle. Using similar reasoning, de Broglie showed that the frequency of the matter wave should be $\nu = E_k/h$, where E_k is the kinetic energy of the particle.

Within three years after de Broglie published his theory of matter waves, two different groups of researchers performed experiments with electrons that supported de Broglie's theory. (One of the physicists who demonstrated the wave nature of electrons was George P. Thomson, the son of J.J. Thomson who had discovered the electron and showed that it is a particle.) The reason that the wave nature of particles had never been observed before de Broglie's work was that large objects have such small wavelengths that any influence that their wave nature might have on their motion is not detectable. For example, a 60 kg sprinter running 10 m/s would have a wavelength of 1.1×10^{-36} m.

De Broglie applied his concept of matter waves to the electrons in the Bohr model of the atom and obtained some remarkable results. He reasoned that the radius of the orbit would have to be equal to an integer number of wavelengths or the waves would cancel themselves out. When he applied his theory of matter waves to calculate the radii of allowed orbits, his results were identical to Bohr's results, lending support to Bohr's model of the atom. However, the more complex line spectra of multi-electron atoms remained unexplained.

The Quantum Mechanical Model of the Atom

De Broglie's matter waves stirred a great deal of interest among the chemists and physicists who were working on an improved model of the atom—one that could explain the line spectra of multi-electron atoms. Erwin Schrödinger, a Viennese physicist, realized that a wave theory and equations were needed for a complete treatment of these "matter waves." In 1926, Schrödinger published an equation that is now known as the Schrödinger wave equation.

When the Schrödinger wave equation is applied to the hydrogen atom, the solution to the equation is a mathematical function called a wave function. This wave function contains three variables that are called quantum numbers, and they are denoted as n , l , and m_l . When you substitute specific combinations of integers for each of these variables into the wave function, you have different solutions to the wave equation. Each solution describes a region in the space around the nucleus of an atom. Each of the quantum numbers represents a specific characteristic of the electrons occupying that space. The atomic model in which electrons are treated as waves is called the **quantum mechanical model of the atom**. Like Bohr's model, the quantum mechanical model limits the energy of an electron to certain discrete values. The region of space that is related to a wave function, or solution to Schrödinger's wave equation, is called an **atomic orbital**.

Shortly after Schrödinger introduced his wave equation, a debate arose among chemists and physicist about the meaning of these matter waves. The currently accepted interpretation was presented by German physicist, Max Born, who showed that the wave functions could be used to determine the probability of finding the electron at any point within the region of space described by the wave function. When the most probable distance from the nucleus is calculated for the electron in the lowest energy level in the hydrogen atom, the result is the same as the Bohr radius, giving validity to both

quantum mechanical model of the atom

an atomic model in which electrons are treated as having wave characteristics

atomic orbital

a region in space around a nucleus that is related to a specific wave function

approaches. As well, the energy of the electron in this lowest energy level, as determined by Schrödinger's wave equation, is the same as the energy calculated by Bohr. However, the solutions to the Schrödinger wave equation provide much more information about electrons in atoms. Nearly all of the observable characteristics of atoms, including their spectra, can be explained by these wave functions. Some refinements, including a fourth quantum number, were soon presented by other chemists and physicists.

Adding credence to the concept of matter waves, in 1927, Werner Heisenberg published a paper in which he mathematically showed that it is not possible to know both the position, x , and momentum (mass times velocity, mv) of a particle with precision. Known as the *Heisenberg uncertainty principle*, this concept can be expressed mathematically as $\Delta x \Delta mv \leq h/4\pi$, where $h/4\pi = 5.2728 \times 10^{-35}$ J·s. The Δ means "a range of values." In other words, you can know that the position, x , of an object is within a certain range Δx , and you can know that its momentum, mv , is within a certain range, Δmv , and the product of those two ranges is $h/4\pi$. As one range becomes smaller, meaning that you know it more precisely, the other range gets larger, to keep the product the same. For large objects, the mass, and thus the momentum, is so large that the ranges within which you can know the position and speed are so small that you can know them precisely. However, the mass of an electron is so small that you cannot know the position, x , or speed, v , with much precision. You can know *only* that the electron is within some region in space, which is essentially what a wave function describes.

You can visualize an atomic orbital as a fuzzy cloud in which the density of the cloud at any point is proportional to the probability of finding the electron at that point. **Figure 3.13** shows the probability map, or orbital, that describes the hydrogen atom in its ground state. Because the cloud has no definite boundary, the "surface" of the cloud is often defined as the region in which the electron spends 90 percent of its time.

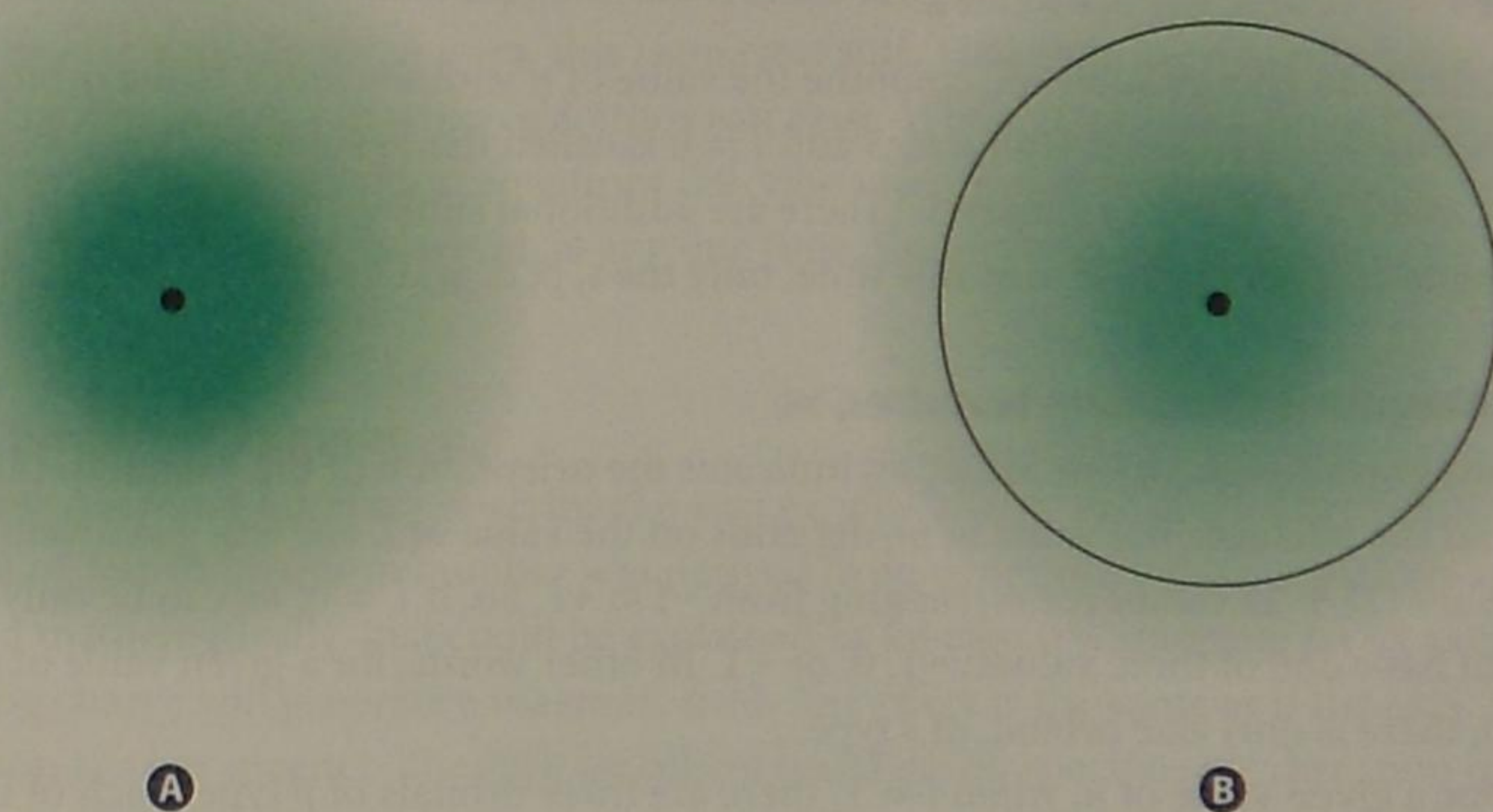


Figure 3.13 The electron density diagram (A) for a hydrogen atom represents the likelihood of locating an electron at a particular point in the atom. The density of the dots at any point is proportional to the probability of finding the electron at that location. The circle (B) shows the region within which the electron spends 90 percent of its time.

Quantum Numbers Describe Orbitals

For the quantum mechanical model of the atom, **quantum numbers** describe electrons in atoms. Three quantum numbers are used to describe the distribution of electrons in the atom. The first quantum number, n , describes an orbital's energy level and relative size. The second quantum number, l , and the third quantum number, m_l , respectively describe an orbital's shape and orientation in space. A fourth quantum number, m_s , describes the behaviour of a specific electron in an orbital.

quantum numbers
integers arising from the solutions to the wave equation that describe specific properties of electrons in atoms

principal quantum number, n a positive whole number (integer) that indicates the energy level and relative size of an atomic orbital

shell the main energy level associated with a given value of n (the principal quantum number)

orbital-shape quantum number, l an integer that describes the shape of atomic orbitals within each principal energy level

sublevel the energy subshell associated with a given value of l (the orbital-shape quantum number)

magnetic quantum number, m_l an integer that indicates the orientation of an orbital in the space around the nucleus

The Principal Quantum Number, n

Recall that the Bohr atomic model uses the symbol n to represent electron orbits. In a similar manner, the quantum mechanical model assigns a **principal quantum number, n** that specifies the energy level, or **shell**, of an atomic orbital and its relative size. All orbitals that have the same value of n are said to be in the same shell. The value of n can range from $n = 1$ to $n = \infty$. The shell with $n = 1$ is called the *first shell*, the shell with $n = 2$ is the *second shell*, and so on. A higher value for n indicates a higher energy level. A greater n value also means that the size of the shell is larger, with a higher probability of finding an electron farther from the nucleus.

The Orbital-Shape Quantum Number, l

Chemists use a variety of names for the second quantum number. In this book, it is referred to as the **orbital-shape quantum number, l** , because it describes an orbital's shape. This quantum number refers to energy **sublevels**, or subshells, within each principal energy level. The values of l are dependent on the value of the principal quantum number, n . The values of l are positive integers that range in value from 0 to $(n - 1)$. So, if $n = 1$, $l = 0$ (that is, $1 - 1$). If $n = 2$, l can be either 0 or 1. If $n = 3$, l can be 0, 1, or 2. Notice that the number of possible values for l in a given energy level is the same as the value of n . In other words, if $n = 2$, then there are only two possible sublevels, or subshells (two types of orbital shapes), at this energy level.

Each value of l is identified by a specific letter— s , p , d , or f —that is used to help distinguish it from the principal quantum number.

- The $l = 0$ orbital has the letter s .
- The $l = 1$ orbital has the letter p .
- The $l = 2$ orbital has the letter d .
- The $l = 3$ orbital has the letter f .

To identify an energy sublevel, combine the value of n with the letter of the orbital shape. For example, the sublevel with $n = 3$ and $l = 0$ is called the $3s$ sublevel. The sublevel with $n = 2$ and $l = 1$ is the $2p$ sublevel. (There are additional sublevels beyond $l = 3$; however, for chemical systems known at this time, only the s , p , d , and f sublevels are required.)

The Magnetic Quantum Number, m_l

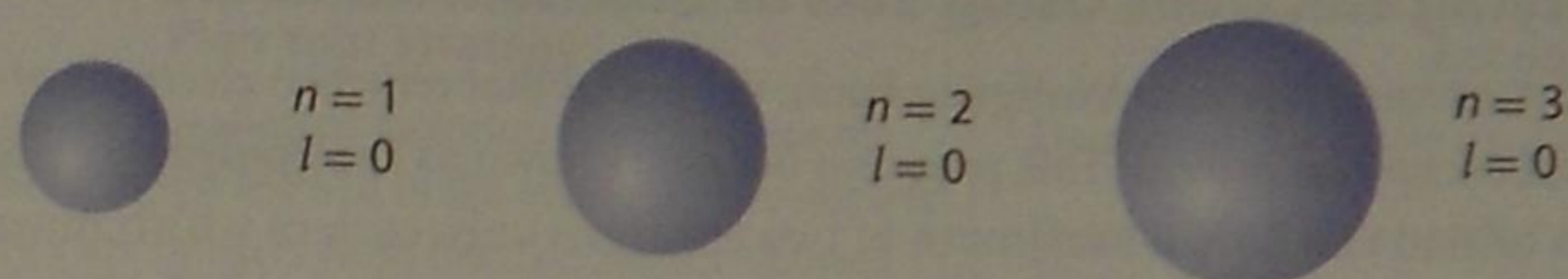
The **magnetic quantum number, m_l** indicates the orientation of the orbital in the space around the nucleus. The value of m_l depends on the value of l . For any given value of l , there are $(2l + 1)$ values for m_l ranging from $-l$ to $+l$. So, if $l = 0$, m_l can be only 0. If $l = 1$, m_l can have one of three values: -1 , 0 , or $+1$. In other words, for a given value of n , when $l = 0$, there is only one orbital, of s type.

For a given value of n , when $l = 1$, there are three orbitals of p type. Each of these p orbitals has the same shape and energy, but a different orientation around the nucleus, and are designated p_x , p_y , and p_z . The total number of orbitals for any energy level n is given by n^2 . For example, if $n = 2$, it has a total of 4 (2^2) orbitals (one s orbital and three p orbitals).

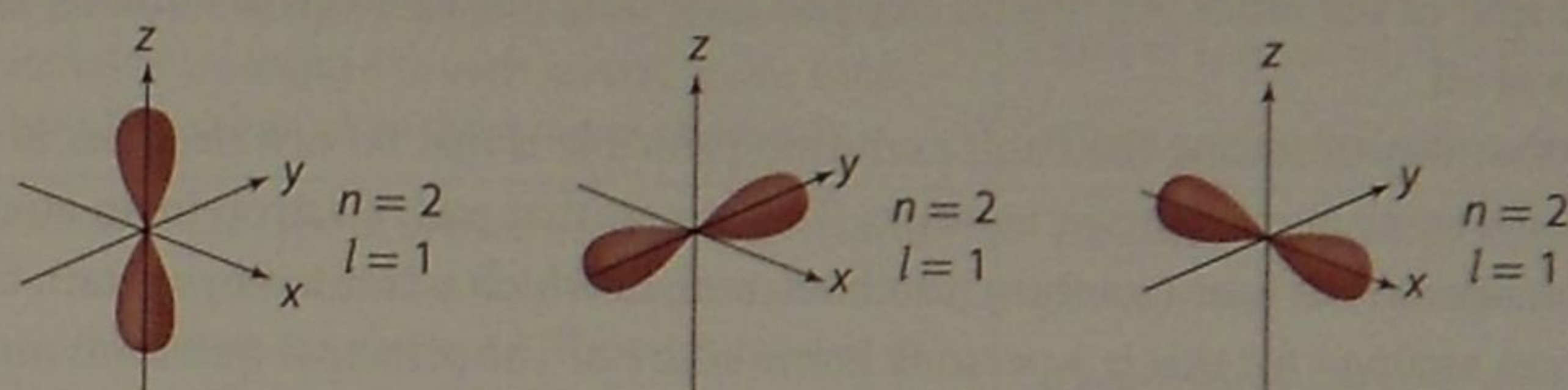
Figure 3.14 shows the shape of the s , p , and d orbitals. The first row shows s orbitals for the first three energy levels, $n = 1$, $n = 2$, and $n = 3$. Notice that the size of the orbital increases as the energy increases, which indicates that the electron spends time farther from the nucleus when it has more energy. The second and third rows show the shapes of the p and d orbitals. (The f orbital shapes are beyond the scope of this chemistry course.)

Keep in mind that the *overall shape* of an atom is a combination of all its orbitals. Thus, the overall shape of an atom is spherical. Be careful, however, to distinguish between the overall spherical shape of the atom and the spherical shape that is characteristic of *only* the s orbitals.

s orbitals



p orbitals



d orbitals

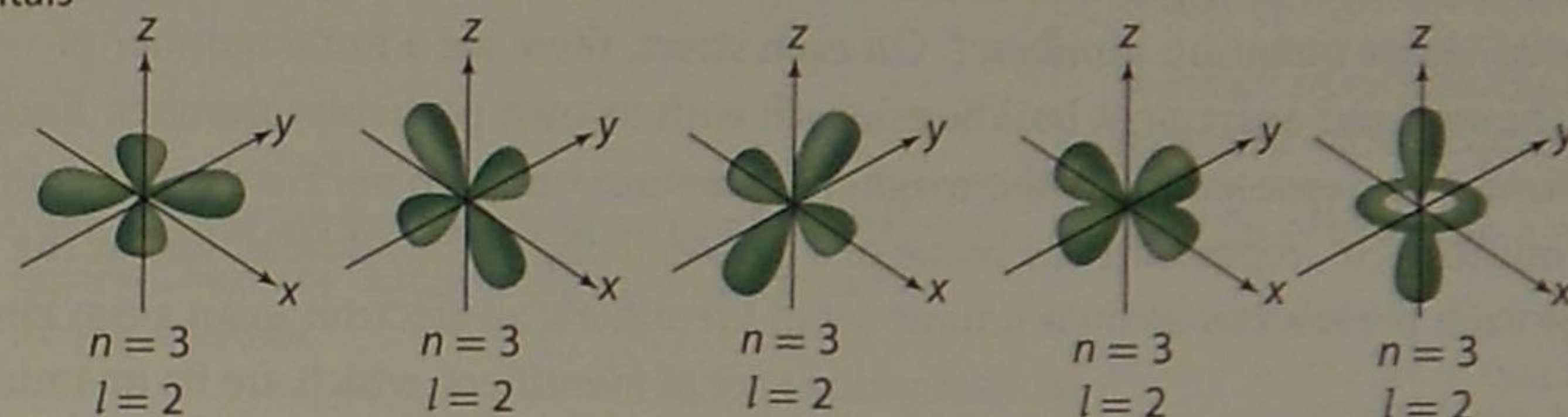


Figure 3.14 All s orbitals are spherical in shape. Each of these p orbitals has a double-lobed shape, but the orientation varies with m_l . Four of the d orbitals have a cloverleaf shape while the fifth looks like a dumbbell with a doughnut around it. These five shapes represent the five values of m_l .

It is also important to be clear that orbitals are solutions to mathematical equations. Those solutions, when manipulated, describe the location of the electron in terms of probabilities. Orbital diagrams in print and electronic resources make orbitals *appear* solid, which can lead to the *misconception* that orbitals are physical “containers” that are “occupied” by electrons. In some ways, this is unavoidable. However, keep in mind that orbitals are regions in space in which electrons *can* exist. When an electron is not there, nothing is there. The mathematical equations describe many possible orbitals for the electron in a hydrogen atom. However, at any one time, the electron occupies only one of those orbitals.

The Spin Quantum Number, m_s

The first three quantum numbers describe the energy, size, shape, and spatial orientation of an orbital. A fourth quantum number was derived from experimental observations and later verified mathematically, that could be explained by an electron spinning on its axis. Any spinning charge will generate a magnetic field. The effect is the same as if the axis of the electron is a bar magnet. The **spin quantum number, m_s** , specifies the direction in which the axis of the electron is oriented and has only two possible values: $+\frac{1}{2}$ or $-\frac{1}{2}$.

Table 3.1 summarizes the four quantum numbers and their properties.

Table 3.1 Summary of Quantum Numbers of Electrons in Atoms

Name	Symbol	Allowed Values	Property
Principal (shell)	n	Positive integers (1, 2, 3, etc.)	Orbital size and energy level
Orbital-shape (subshell)	l	Integers from 0 to $(n - 1)$	Orbital shape (l values 0, 1, 2, and 3 correspond to s, p, d, and f orbitals)
Magnetic	m_l	Integers from $-l$, to $+l$	Orbital orientation
Spin	m_s	$+\frac{1}{2}$ or $-\frac{1}{2}$	Spin orientation

spin quantum number, m_s the quantum number that specifies the orientation of the axis on which the electron is spinning

Pauli exclusion principle a principle that states that a maximum of two electrons can occupy an orbital, and that the electrons must have opposite spins

Identifying Electrons Using Sets of Quantum Numbers

In 1925, Austrian physicist, Wolfgang Pauli, proposed that *only two electrons of opposite spin could occupy an orbital*. This proposal became known as the **Pauli exclusion principle**. Thus, an orbital can have a maximum of two electrons only, each of which must have the opposite spin of the other. An orbital can also have only one electron of either spin or no electrons at all.

Another way of stating the Pauli exclusion principle is that *no two electrons in an atom can have the same four quantum numbers*. This means that each electron in an atom has its own unique set of four quantum numbers, each of which is limited by certain factors. A common analogy for this is a person's home address. The principal quantum number, n , represents a city. In the city, there are a finite number of streets. Each street is represented by the orbital-shape quantum number, l . On each street, there are a finite number of buildings (houses and apartment buildings), each with its own particular number. Each building number is represented by the magnetic quantum number, m_l . Finally, the spin quantum number, m_s , represents the name of a person living at the address. Just as the address for each person has its own unique set of identifiers, an electron in an atom has

its own unique set of identifiers, which are its quantum numbers. In general, in any energy level, n , there can be no more than $2n^2$ electrons.

Table 3.2 provides the set of quantum numbers that distinguish between the ground-state hydrogen atom and helium atom. Recall that a helium atom has two electrons. Note also that the m_s quantum number is given as $+\frac{1}{2}$. It could just as easily have a value of $-\frac{1}{2}$. By convention, chemists usually use the positive value first.

Table 3.2 Quantum Numbers for Hydrogen and Helium

Atom	Electron	Quantum Numbers
hydrogen	Lone	$n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$
helium	First	$n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$
	Second	$n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$

Sample Problem

Determining Quantum Numbers

Problem

- What values of l and m_l are allowed for a principal quantum number, n , of 2? How many orbitals exist for $n = 2$?
- Give the possible values for m_l if $n = 4$ and $l = 3$. What type of orbital is associated with these quantum numbers? How many orbitals are associated with these quantum numbers?
- What is the set of quantum numbers for one electron in the 3s orbital?

What Is Required?

- You need to determine the allowed values for l and m_l , and the number of orbitals that exist, for a principal quantum number of $n = 2$.
- You need to determine the type of orbital, and the number of orbitals, associated with the quantum numbers $n = 4$ and $l = 3$.
- You need to determine n , l , m_l , and m_s for an electron in the 3s orbital.

What Is Given?

- You are given the value of the principal quantum number as $n = 2$.
- You are given the values of the quantum numbers, $n = 4$ and $l = 3$.
- You are given the electron orbital, 3s.

Plan Your Strategy	Act on Your Strategy
a. To determine the allowed quantum numbers, use the rules you have just learned in the textbook. The allowed values for l are integers from 0 to $(n - 1)$. The allowed values for m_l are integers from $-l$ to $+l$, including 0. One m_l value is assigned to each orbital, so the total number of m_l values gives the number of orbitals.	Determining l values for $n = 2$: $l = 0, 1$ Determining m_l for each l value: for $l = 0$, $m_l = 0$ for $l = 1$, $m_l = -1, 0, +1$ There are four m_l values, so there are four orbitals with $n = 2$.
b. To determine the type of orbital, combine the value for n with the letter used to identify l . You can determine the possible values for m_l from l . The total number of m_l values gives the number of orbitals.	Determining the type of orbital, the $l = 3$ orbital has the letter f . Since $n = 4$, the quantum numbers represent a $4f$ orbital. Determining the total number of orbitals, find m_l for $l = 3$: m_l may be $-3, -2, -1, 0, +1, +2, +3$. There are seven possible m_l values, so there are seven orbitals associated with the quantum numbers.
c. To determine the four quantum numbers for the electron, begin by determining which are possible for the $3s$ orbital.	Since the orbital is $3s$: $n = 3$, $l = 0$, and $m_l = 0$. Since there is one electron and by convention it is assigned a $m_s = +\frac{1}{2}$, the set of quantum numbers for the electron is $n = 3$, $l = 0$, $m_l = 0$, and $m_s = +\frac{1}{2}$.

Check Your Solution

- Since the total number of orbitals for any given n is n^2 , when $n = 2$, the number of orbitals must be 4 (that is, 2^2).
- The number of m_l values is equivalent to $2l + 1$: $2(3) + 1 = 7$. Since the number of orbitals equals the number of m_l values, the answer of 7 must be correct.
- Since it is an s orbital, there can only be a maximum of 2 electrons. These would have the same first three quantum numbers and differ only by the spin quantum number, m_s .

Practice Problems

- For the quantum number $n = 3$, what values of l are allowed, what values of m_l are possible, and how many orbitals are there?
- If $n = 5$ and $l = 2$, what orbital type is this, what are the possible values for m_l , and how many orbitals are there?
- What are the n , l , and possible m_l values for the following orbital types?
 - $2s$
 - $3p$
 - $5d$
 - $4f$
- What orbital type can be described by the following sets of quantum numbers?
 - $n = 2$, $l = 0$, $m_l = 0$
 - $n = 5$, $l = 3$, $m_l = -2$
- How many orbitals are associated with each of the following types?
 - $1s$
 - $5f$
 - $4f$
 - $2p$
- What sets of quantum numbers are possible for a $4d$ orbital? List them.
- What is one possible value for the missing number in each of the following sets?
 - $n = 3$, $l = 1$, $m_l = ?$
 - $n = 2$, $l = ?$, $m_l = -3$
- Write two possible sets of quantum numbers for a $6p$ orbital.
- The following sets of quantum numbers are not allowed. Identify the problem and change one number to give an allowed set.
 - $n = 1$, $l = 2$, $m_l = -2$
 - $n = 4$, $l = 1$, $m_l = -2$
- Label each of the following sets of quantum numbers as *allowed* or *not allowed*. Identify the problem for each of the *not allowed* sets.
 - $n = 3$, $l = 2$, $m_l = 0$
 - $n = 1$, $l = 1$, $m_l = -1$
 - $n = 0$, $l = 0$, $m_l = 0$
 - $n = 5$, $l = 1$, $m_l = 3$

Section Summary

- According to the quantum mechanical model of the atom, electrons have both matter-like and wave-like properties.
- The position and motion of electrons cannot both be determined with certainty, so the position is described in terms of probabilities.
- An orbital represents a mathematical description of the volume of space around a nucleus in which an electron has a probability of being found.
- The first three quantum numbers describe the size, energy, shape, and orientation of an orbital. The fourth quantum number describes the orientation of the axis around which the electron is spinning.

Review Questions

- K/U** How does n in Bohr's atomic model compare to n in the quantum mechanical model of the atom?
- C** Draw a diagram to show the allowed values for l and m_l when $n = 4$.
- K/U** What is the name and symbol of the fourth quantum number, what values can it have, and what property does it represent?
- C** Construct and complete a table to show key characteristics of the quantum numbers n , l , m_l , and m_s .
- C** Think of visual analogies to help you remember the shapes of the s , p , and d orbitals. For example, the p orbital might remind you of barbells. Sketch a diagram to show your analogies.
- T/I** Agree or disagree with the following analogy, and support your opinion: An electron in an orbital is like a fly trapped in a glass jar.
- A** Label each of the following sets of quantum numbers as *allowed* or *not allowed*. Identify the problem for each of the *not allowed* sets.
 - $n = 2, l = 2, m_l = 0$
 - $n = 2, l = 0, m_l = -1$
 - $n = 4, l = 0, m_l = 0$
 - $n = 2, l = 3, m_l = -1$
- T/I** How many of each of the following types of orbitals are there in an atom?

a. $3s$	d. $7d$
b. $7f$	e. $2s$
c. $4p$	f. s
- T/I** How many sets of quantum numbers are possible for a $3p$ orbital? List them.
- T/I** What is wrong with each set of quantum numbers? Change one number to give an allowed set.
 - $n = 0, l = 1, m_l = 0$
 - $n = 3, l = 2, m_l = -3$
- C** A friend missed the class in which orbitals were discussed. Write a brief e-mail to explain what an orbital is.
- T/I** Examine **Figure 3.14**. In what key ways do d orbitals differ from s and p orbitals?
- A** A classmate says, "Since there are $2n^2$ electrons possible in each energy level, and the atom with the greatest number of electrons has 118 electrons, that must mean that 8 is the highest possible value for n , because a value of 7 gives $2n^2 = 98$ and a value of 8 gives $2n^2 = 128$."
 - State two problems with this reasoning.
 - How many energy levels are there for a given atom?
- K/U** If the $n = 1$ energy level is shown in a diagram as a sphere, what does this sphere represent?
- K/U** What is the Pauli exclusion principle and what consequence does it have in terms of quantum numbers?
- T/I** Is it possible for a hydrogen atom's one electron to have the following quantum numbers: $n = 2, l = 0, m_l = 0, m_s = +\frac{1}{2}$? Explain your answer.
- K/U** How does $n = 2$ compare with $n = 1$ in terms of its size and the energy of an electron moving in its volume?
- T/I** What is the greatest number of electrons possible in each of the following energy levels?

a. $n = 1$	c. $n = 3$
b. $n = 2$	d. $n = 4$
- K/U** Explain why there are $(2l + 1)$ values for m_l for any given value of l .
- A** Given the information that an electron is associated with $l = 0$, can you tell what the value of n is? Explain your answer.

SECTION 3.3

Electron Configurations and the Periodic Table

The single-electron atom, hydrogen, is unique with respect to the energies of its orbitals, because the energy for any given orbital depends only on n , the principal quantum number. For example, consider a situation in which a hydrogen atom is excited by an electric current in a gas discharge tube. As a result of this absorption of energy, the electron jumps to the $n = 4$ level. In the fourth energy level, there is no difference in the energy of the electron if it is in the $4s$, $4p$, $4d$, or $4f$ orbital. An electron in any orbital of the fourth energy level, or shell, will have the same energy. The situation is quite different, however, for atoms with two or more electrons. Electrons in different orbitals within the same energy level will have different energies.

Key Terms

electron configuration
orbital diagram
aufbau principle
Hund's rule
atomic radius
ionization energy
electron affinity

Atomic Orbital Energies for Many-Electron Atoms

To understand why the presence of more than one electron in an atom affects the energies of electrons in different orbitals within the same energy level, examine **Figure 3.15**. First look at **Figure 3.15A**, which shows the interaction between the nucleus and the electron in the single-electron atom, hydrogen. The attractive force between the positively charged nucleus and the negatively charged electron is the only interaction occurring in the atom. This interaction is incorporated into the Schrödinger wave equation when solving it for hydrogen. The solutions give results for all possible combinations of quantum numbers. Analysis shows that, regardless of the degree of excitation, there will be no difference in the energy of an electron whether it is in the s , p , d , or f orbitals for any specific n .

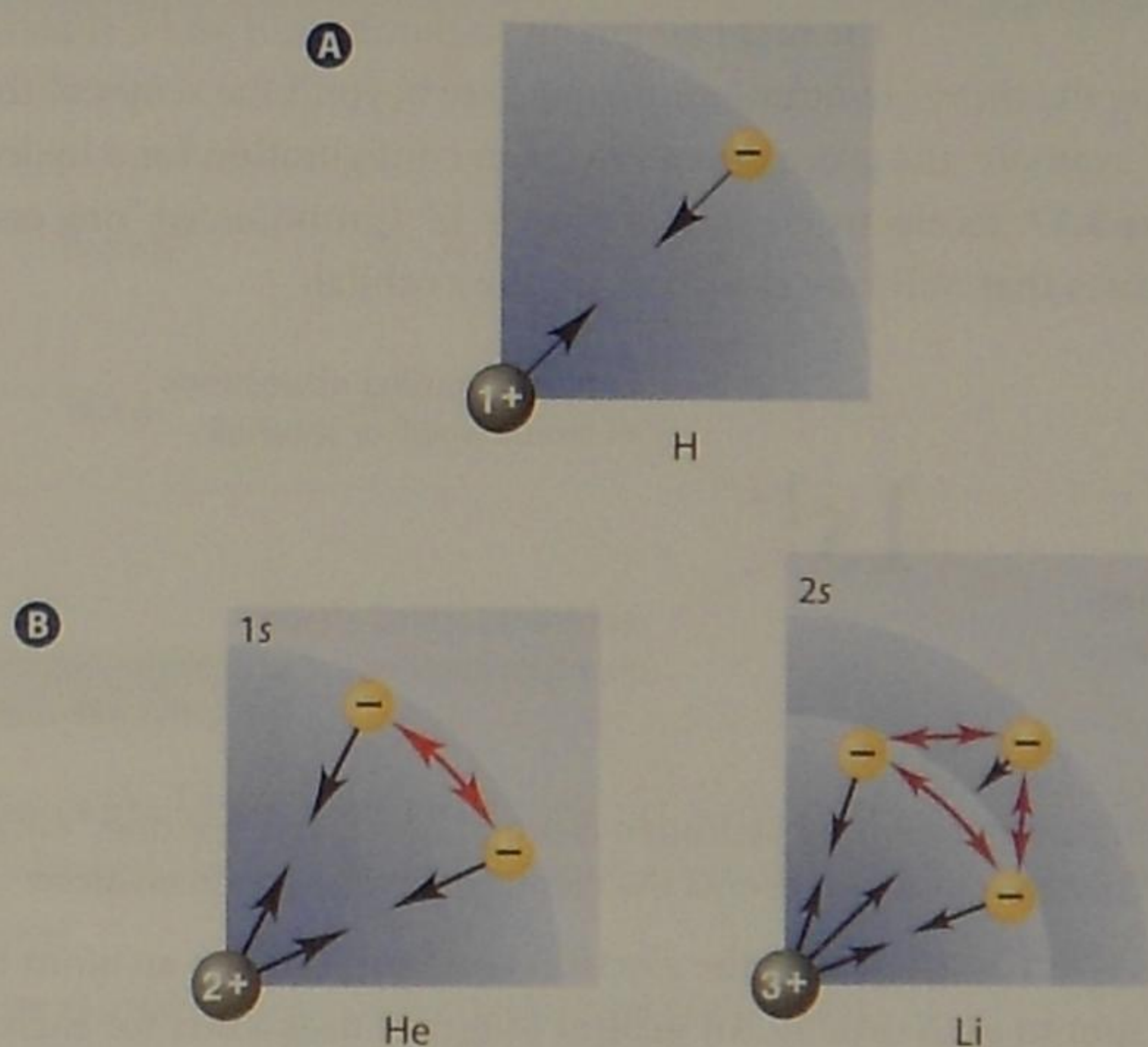


Figure 3.15 In the hydrogen atom (A), the only force affecting the electron is the attractive force between the nucleus and the electron. In helium (B) and Li (C) atoms, each electron is attracted by the nucleus and repulsed by the other electrons in the atom.

Now focus on **Figure 3.15B**, which shows the helium and lithium atoms. There are attractive forces between the nucleus and each of the electrons, as well as repulsive forces between each of the electrons of the atom. All of these interactions must be incorporated into the Schrödinger wave equation to solve it for these atoms. Not only the nucleus, but also all of the other electrons influence the energy of any individual electron in its orbital. As a result, the energies of the s , p , d , and f orbitals within the same shell (same value of n) are different. This difference in the energies of the orbitals is shown in what is called an energy level diagram for multi-electron atoms in **Figure 3.16**. One reason for the difference in the energies of electrons in these orbitals is that electrons in an s orbital—for example, the $2s$ orbital—spend more time closer to the nucleus than do the electrons in the $2p$ orbitals. Thus, the energy level of the $2s$ electrons is lower than that of the $2p$ electrons.

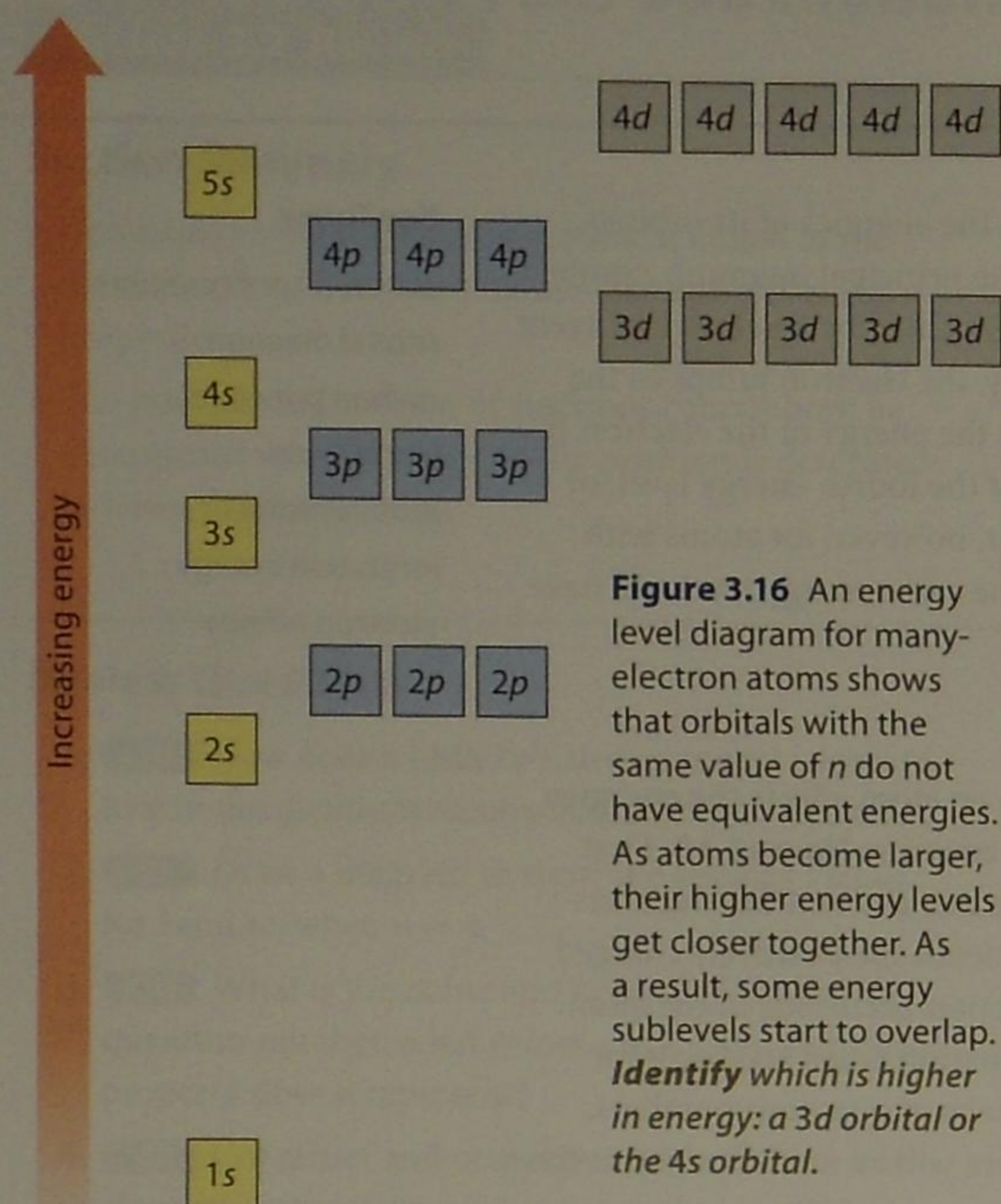


Figure 3.16 An energy level diagram for many-electron atoms shows that orbitals with the same value of n do not have equivalent energies. As atoms become larger, their higher energy levels get closer together. As a result, some energy sublevels start to overlap. **Identify which is higher in energy: a 3d orbital or the 4s orbital.**

As you can see, in the energy level diagram in **Figure 3.16**, the 2s orbital has a lower energy than the 2p orbitals. Similarly, the 3p orbitals are lower in energy than the 3d orbitals. Notice, however, that all the orbitals within a sublevel have the same energy. For example, the three p orbitals in the 3p sublevel have the same energy. As you learn to describe the distribution of electrons in many-electron atoms, refer to this diagram or the order of orbital energy below.

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < \dots$$

Representing Electrons: Electron Configurations and Orbital Diagrams

An atom's **electron configuration** shows the number and arrangement of electrons in its orbitals. Since the value of n ranges to infinity, each atom has an infinite number of possible electron configurations. By convention, electron configurations are drawn with the atoms in their lowest possible energy levels, because an atom's chemical properties are mainly associated with its ground-state electron configuration.

Electron configurations provide information about the first two quantum numbers, n and l . (Electron

configurations reflecting the third quantum number, m_l , are beyond the scope of this chemistry course.) For example, the ground-state electron configuration for a hydrogen atom is shown in **Figure 3.17**. Its electron configuration is $1s^1$ (pronounced "one ess one"). The superscript 1 indicates that only one electron is in the s orbital.

electron configuration a shorthand notation that shows the number and arrangement of electrons in an atom's orbitals

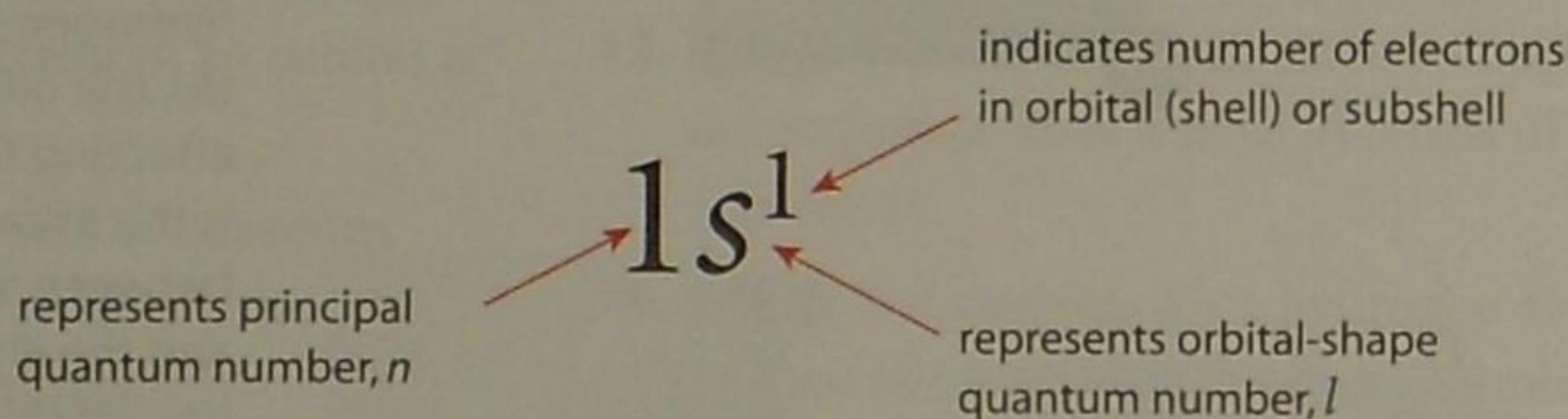


Figure 3.17 The electron configuration for hydrogen is pronounced "one ess one." Each number and letter in an electron configuration represents the electron distribution in an atom.

An orbital diagram often accompanies the electron configuration for an atom to represent the electron spin in each orbital. An **orbital diagram** uses a box for each orbital in any given principal energy level. (Some chemists use a circle or a line instead of a box.) An empty box represents an orbital with no electrons (an unoccupied orbital). A box that has a single arrow represents an orbital that is half-filled. A box with two oppositely pointing arrows represents a filled orbital. **Figure 3.18** shows how electron configuration and orbital diagrams are represented together.

orbital diagram a diagram that uses a box for each orbital in any given principal energy level

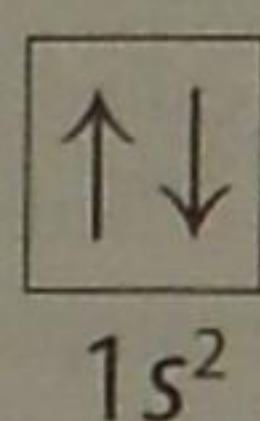


Figure 3.18 The ground-state electron configuration for a helium atom is $1s^2$ (pronounced "one ess two", not "one ess squared"). The superscript 2 indicates that there are two electrons in the s orbital. The opposite arrows in the orbital diagram indicate that the electrons are of opposite spins.

Describing the Electrons in Lithium

An orbital can have a maximum of two electrons, and they must have opposite spins. This principle applies when writing electron configurations and orbital diagrams. **Table 3.3** summarizes how electrons in lithium (Li), which has three electrons, are described using quantum numbers, electron configuration notation, and an orbital diagram.

For lithium, the first two electrons occupy the 1s orbital. According to the Pauli exclusion principle, the 1s orbital ($n = 1$) is full, because it contains the maximum number of electrons: 2. For lithium's third electron, n cannot equal 1. Therefore, the next principal energy level for the electron is $n = 2$. If $n = 2$, l may have a value of 0 or 1. Because an orbital with $l = 0$ (an s orbital) has a lower energy than an orbital with $l = 1$ (a p orbital), you would expect a high probability of finding lithium's third electron in the s orbital given by $n = 2$, $l = 0$. In fact, experimental evidence supports this expectation. You know that if $l = 0$, m_l has only one possible value: 0. Finally, by convention, m_s is $+\frac{1}{2}$. The electron configuration shows two of the electrons in the 1s orbital and the third in the next energy level, 2s. For the orbital diagram, the filled 1s orbital is shown as a pair of opposite arrows, and by convention the one electron in the 2s orbital is pointing upwards, which represents a positive m_s .

You may have noticed that the first few examples of electron configurations do not include information about the spin direction of the electron. Once you have seen the electron configurations for a variety of atoms, you will see that you can safely infer where electrons with opposite spins have been paired.

Table 3.3 Descriptions of Electrons in Lithium

Atom	Electron	Quantum Numbers	Electron Configuration	Orbital Diagram
lithium	First	$n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$	$1s^2 2s^1$	
	Second	$n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$		
	Third	$n = 2, l = 0, m_l = 0, m_s = +\frac{1}{2}$		

Learning Check

- What is the key difference between the orbitals of a hydrogen atom and the orbitals of multi-electron atoms?
- Write the following sets of orbitals in order from lowest to highest energy.
 - 2s, 2p, 3s, 3p
 - 3p, 3d, 4s, 4p
 - 4d, 4f, 5s, 5p, 5d, 5f, 6s, 6p
- What does it mean to say that an orbital is "full"?
- How many electrons can occupy all possible orbitals with $n = 1$ and $n = 2$? Show two ways to arrive at the answer.
- The orbital diagram for helium is given in **Figure 3.18**. Would drawing two arrows pointing in the same direction also be a correct orbital diagram? Explain your answer.
- Draw an orbital diagram to represent each of the following:
 - an "unoccupied" orbital
 - an orbital with a single electron
 - a filled orbital

Writing Electron Configurations and Orbital Diagrams

Electron configurations are closely related to the structure of the periodic table. To write electron configurations, start with the first element in the periodic table and “build up” its electronic configuration by adding an electron to its lowest available energy level. Then turn your attention to the next element, which has one more proton in the nucleus, and add an electron to the appropriate orbital. This process of building up the ground-state electronic structure for each atom, in order of atomic number, is called the aufbau principle. (*Aufbau* comes from a German word that means “to build up.”) The **aufbau principle** states that *each electron occupies the lowest energy orbital available*.

To start representing the electron structures of atoms, you will use both electron configurations and orbital diagrams. Refer to the following guidelines and the relative energies of orbitals as you work your way through the information that follows.

Guidelines for “Filling” Orbitals

1. Place electrons into the orbitals in order of increasing energy level.
2. Completely fill orbitals of the same energy level before proceeding to the next orbital or series of orbitals.
3. When electrons are added to orbitals of the same energy sublevel, each orbital receives one electron before any pairing occurs.
4. When electrons are added individually to different orbitals of the same energy, the electrons must all have the same spin.

Guidelines 3 and 4 reflect **Hund's rule**, which states that *single electrons with the same spin must occupy each equal-energy orbital before additional electrons with opposite spins can occupy the same orbitals*. For example, **Figure 3.19** shows the sequence in which six electrons occupy three p orbitals. One electron enters each of the three p orbitals before a second electron enters any orbitals.

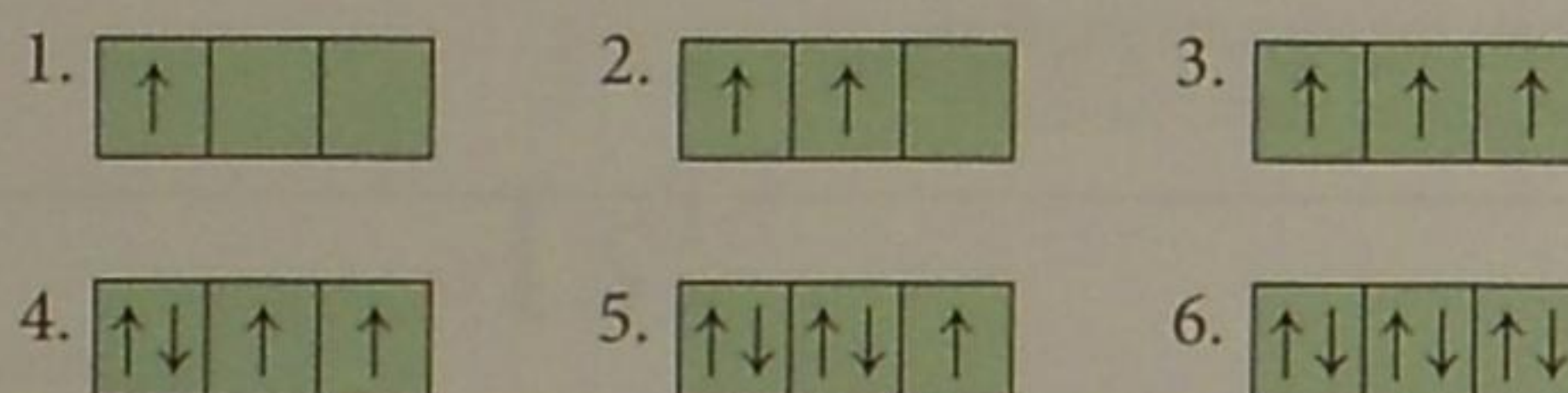


Figure 3.19 The three boxes represent each of the $2p$ orbitals. Electrons are “added” one at a time to each orbital. When each orbital has one electron, a second electron is added.

Filling Orbitals for Periods 1 and 2











Table 3.4 shows orbital diagrams and electron configurations for elements 1 to 10. Note the following:

- To draw orbital diagrams, place the electron in the first available box, from left to right.
- The energy of each orbital (or group of orbitals) increases from left to right.
- Boron's fifth electron goes into the $2p$ energy sublevel. Since $l = 1$, m_l may be -1 , 0 , or $+1$. The fifth electron can go into any of these orbitals, since they have the same energy.
- By convention, electrons are placed in the orbital boxes from left to right.
- With carbon, you must apply Hund's rule. That is, carbon's sixth electron must go into the next unoccupied $2p$ orbital. (Experimental evidence confirms this configuration.)
- The Pauli exclusion principle applies to oxygen. As with helium's $1s$ orbital and beryllium's $2s$ orbital, the last-added (eighth) electron is paired with a $2p$ electron of opposite spin.

aufbau principle a principle behind an imaginary process of building up the electronic structure of the atoms, in order of atomic number

Hund's rule a rule stating that the lowest energy state for an atom has the maximum number of unpaired electrons allowed by the Pauli exclusion principle in a given energy sublevel

Table 3.4 Orbital Diagrams and Electron Configurations for the First Ten Elements

Atomic Number (Z)	Element	Orbital Diagram	Electron Configuration	Orbital Shape*
1	H	$\boxed{\uparrow}$ 1s	$1s^1$	
2	He	$\boxed{\uparrow\downarrow}$ 1s	$1s^2$	
3	Li	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{}$ $\boxed{}$ 1s 2s 2p	$1s^2 2s^1$	
4	Be	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{}$ $\boxed{}$ 1s 2s 2p	$1s^2 2s^2$	
5	B	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{}$ $\boxed{}$ 1s 2s 2p	$1s^2 2s^2 2p^1$	
6	C	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ $\boxed{}$ 1s 2s 2p	$1s^2 2s^2 2p^2$	
7	N	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ 1s 2s 2p	$1s^2 2s^2 2p^3$	
8	O	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ 1s 2s 2p	$1s^2 2s^2 2p^4$	
9	F	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ 1s 2s 2p	$1s^2 2s^2 2p^5$	
10	Ne	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ 1s 2s 2p	$1s^2 2s^2 2p^6$	

* Orbital occupancy is indicated with shading. The lighter colour indicates half-filled orbitals; the darker colour indicates filled orbitals.

Filling Orbitals for Period 3

Writing electron configurations and drawing orbital diagrams for atoms of Period 3 elements follows the same process as for Period 2. However, a *condensed electron configuration* is used to reduce the length of the electron configurations. This condensed notation places the electron configuration of the noble gas of the previous period in square brackets, using its atomic symbol only. Then you continue with the configuration of the next energy level being filled. For example, the condensed electron configuration for a nitrogen atom is $[\text{He}]2s^2 2p^3$. The notation $[\text{He}]$ is used to represent $1s^2$. For a sodium atom ($Z = 11$), the condensed electron configuration is $[\text{Ne}]3s^1$. Here, $[\text{Ne}]$ represents $1s^2 2s^2 2p^6$. Orbital diagrams that accompany these condensed electron configurations are also partial orbital diagrams. Only the valence electrons are represented in the diagrams.

For the transition and Group 12 elements, the “next energy level being filled” does not correspond to orbitals with the same principal quantum number. Referring to **Figure 3.16**, you can see that d electrons with one principal quantum number have energies between the s and p orbitals corresponding to the next principal quantum number. For example, for Period 4 elements, the energy levels being filled consist of the $4s$ electrons, the $3d$ electrons, and the $4p$ electrons in that order. For the transition elements, the $(n - 1)d$ electrons, as well as the ns electrons are considered valence electrons.

Suggested Investigation

Inquiry Investigation 3-B,
Electronic Structures for
Period 3 Elements

Filling Orbitals for Period 4

As discussed above, electrons start occupying $3d$ orbitals *only* when the $4s$ orbital has been filled. **Table 3.5** shows electron configurations and partial orbital diagrams for the Period 4 elements. The guidelines you have been using can help you write correct ground-state electron configurations for all elements up to and including vanadium (atomic number 23). After this point, two apparent exceptions occur: chromium and copper. Experimental evidence supports the idea that the energy of orbitals can change as electrons are added. In these cases, when all of the d orbitals are half-filled, as in chromium, or completely filled, as in copper, the atoms are more stable than if the s orbitals were filled. The correct configurations for chromium and copper, respectively, are $[\text{Ar}]4s^1 3d^5$ and $[\text{Ar}]4s^1 3d^{10}$. Similar situations arise for a number of atoms in the remaining periods.

Table 3.5 Orbital Diagrams and Electron Configurations for Period Four Elements

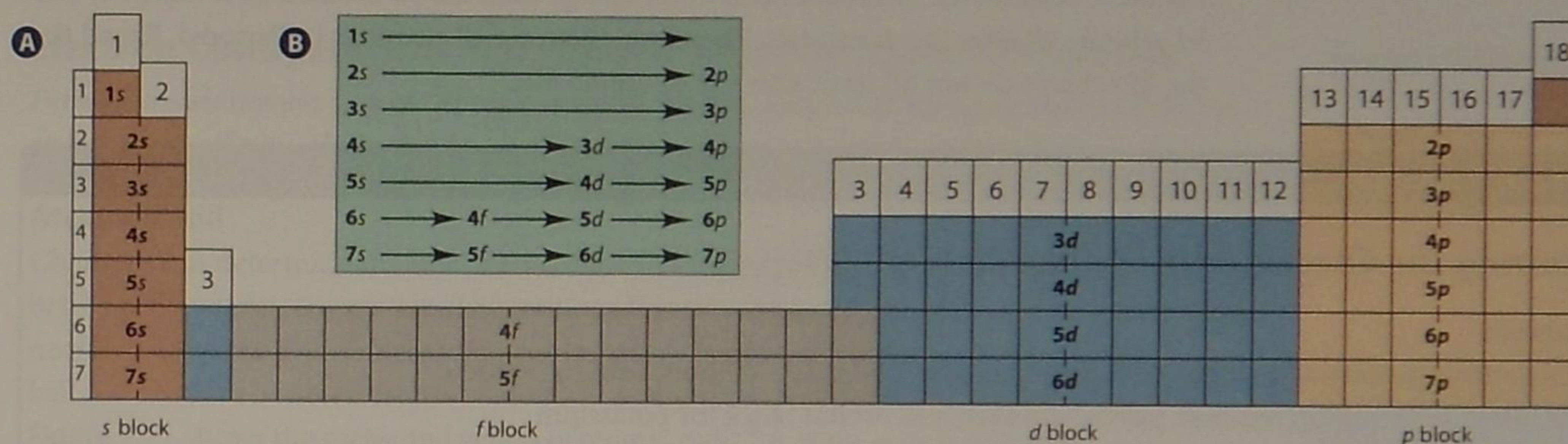
Atomic Number (Z)	Element	Orbital Diagram	Condensed Electron Configuration
19	K	$4s$ \uparrow $3d$ $4p$	$[\text{Ar}]4s^1$
20	Ca	$4s$ $\uparrow\downarrow$ $3d$ $4p$	$[\text{Ar}]4s^2$
21	Sc	$4s$ $\uparrow\downarrow$ $3d$ \uparrow $4p$	$[\text{Ar}]4s^2 3d^1$
22	Ti	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\uparrow$ $4p$	$[\text{Ar}]4s^2 3d^2$
23	V	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\uparrow\uparrow$ $4p$	$[\text{Ar}]4s^2 3d^3$
24	Cr	$4s$ \uparrow $3d$ $\uparrow\uparrow\uparrow\uparrow\uparrow$ $4p$	$[\text{Ar}]4s^1 3d^5$
25	Mn	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\uparrow\uparrow\uparrow\uparrow$ $4p$	$[\text{Ar}]4s^2 3d^5$
26	Fe	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\downarrow\uparrow\uparrow\uparrow\uparrow$ $4p$	$[\text{Ar}]4s^2 3d^6$
27	Co	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\downarrow\uparrow\downarrow\uparrow\uparrow\uparrow$ $4p$	$[\text{Ar}]4s^2 3d^7$
28	Ni	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\uparrow$ $4p$	$[\text{Ar}]4s^2 3d^8$
29	Cu	$4s$ \uparrow $3d$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ $4p$	$[\text{Ar}]4s^1 3d^{10}$
30	Zn	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ $4p$	$[\text{Ar}]4s^2 3d^{10}$
31	Ga	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ $4p$ \uparrow	$[\text{Ar}]4s^2 3d^{10} 4p^1$
32	Ge	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ $4p$ $\uparrow\uparrow$	$[\text{Ar}]4s^2 3d^{10} 4p^2$
33	As	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ $4p$ $\uparrow\uparrow\uparrow$	$[\text{Ar}]4s^2 3d^{10} 4p^3$
34	Se	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ $4p$ $\uparrow\downarrow\uparrow\uparrow$	$[\text{Ar}]4s^2 3d^{10} 4p^4$
35	Br	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ $4p$ $\uparrow\downarrow\uparrow\downarrow\uparrow$	$[\text{Ar}]4s^2 3d^{10} 4p^5$
36	Kr	$4s$ $\uparrow\downarrow$ $3d$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ $4p$ $\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$[\text{Ar}]4s^2 3d^{10} 4p^6$

Learning Check

- Why do electrons fill the $5s$ orbital before the $4d$?
- Write full and condensed electron configurations and orbital diagrams for boron and neon.
- Write the complete electron configuration for sulfur.
- Draw a partial orbital diagram for silicon in the ground state.
- Identify the elements with these condensed electron configurations, and write the complete forms.
 - $[\text{Ne}]3s^1$
 - $[\text{Ar}]4s^23d^3$
- Identify the following element, and write a condensed electron configuration for it.
 $1s^22s^22p^63s^23p^64s^23d^2$

Using the Periodic Table to Predict Electron Configurations

The periodic table in **Figure 3.20** has segments colour-coded and labelled according to the type of orbital being filled. **Figure 3.20B** highlights the filling order, and therefore the energy order, of the orbitals when you read the periodic table from left to right. Note that Period 1 contains only s -block elements, Periods 2 and 3 contain both s - and p -block elements, Periods 4 and 5 contain s -, p -, and d -block elements, and Periods 6 and 7 contain s -, p -, d -, and f -block elements.



s-Block Elements

The s block consists of Groups 1 and 2. Valence electrons occupy only the s orbitals. Group 1 elements have partially filled s orbitals and electron configurations ending in ns^1 . Group 2 elements have completely filled s orbitals and electron configurations ending in ns^2 . Since the s orbitals can hold a total of two electrons, s block elements span two groups.

p-Block Elements

The p block contains Groups 13 to 18, and its elements have filled or partially filled p orbitals. The electron configuration of Group 18 elements takes the general form ns^2np^6 , representing fully occupied s and p orbitals. Because the three p orbitals can hold a maximum of six electrons, the p block elements span six groups.

d-Block Elements

The d block contains the transition metal elements, as well as Group 12 of the main group elements. Apart from a few exceptions, d -block elements have filled s orbitals and filled or partially filled d orbitals of energy level $n - 1$. Because the five d orbitals can hold a maximum of 10 electrons, the d block spans 10 groups.

f-Block Elements

The f block includes the inner transition elements. These atoms have filled s orbitals in the outer energy levels and filled or partially filled $4f$ and $5f$ orbitals. In general, the notation for the orbital filling sequence for Period 6 and Period 7 is ns , followed by $(n - 2)f$, then $(n - 1)d$, and np . However, many exceptions make predictions difficult. Because there are seven f orbitals, with a maximum of 14 electrons, the f block spans 14 groups.

Figure 3.20 The periodic table can be divided (A) into four regions, the s block, p block, d block, and f block, according to the four energy sublevels. If you "read" the periods like the words on a page (B), the elements are arranged into sublevel blocks that occur in the order of increasing energy.

Group and Period Numbers Provide Patterns

Elements in a group have similar outer electron configurations and the same number of valence electrons, so they have similar chemical properties. This gives rise to three patterns:

- For main-group elements, the last numeral of the group number is the same as the number of valence electrons. For example, phosphorus in Group 15 has five valence electrons. Strontium in Group 2 has two valence electrons. The exception to this pattern is helium with its outermost energy level fully occupied by two valence electrons.
- The n value of the highest occupied energy level is the period number. For example, atoms of elements that have electrons with $n = 3$ appear in Period 3. Atoms of elements that have electrons with $n = 6$ appear in Period 6.
- The square of the n value (n^2) equals the total number of orbitals in that energy level. In addition, since each orbital can have a maximum of two electrons, the maximum number of electrons in any principal energy level is $2n^2$. For example, with $n = 2$, there are four orbitals: one $2s$ orbital and three $2p$ orbitals. Squaring the n value gives $2^2 = 4$. The total number of electrons in this energy level is *eight*, given by $2n^2$, and notice that there are *eight* elements in Period 2. For Period 3 elements, $n = 3$, and the number of orbitals is $n^2 = 9$. The number of electrons is $2n^2 = 18$. However, there are only eight elements in Period 3, because the $4s$ orbital has a lower energy than the $3d$ orbitals, so it fills first. The $3d$ orbitals fill after the $4s$ orbitals. Therefore, there are 18 elements in Period 4. Recall that the $4f$ orbitals do not fill until after the $6s$ orbital fills.

Sample Problem

Inferring the Characteristics of an Element

Problem

The condensed electron configuration for potassium is $[\text{Ar}]4s^1$. Without using a periodic table, identify the group number, period number, and orbital block for potassium.

What Is Required?

You need to use the condensed electron configuration to deduce the characteristics (group number, period number, and orbital block) of potassium.

What Is Given?

The condensed electron configuration for the potassium atom is given as $[\text{Ar}]4s^1$.

Plan Your Strategy	Act on Your Strategy
From the electron configuration, you can infer the energy level of the valence electrons, which tells you the period number for potassium. The number of valence electrons and their sublevel enable you to infer the group number and the block.	The configuration for the valence electrons, s^1 , indicates that potassium is in Group 1. The value of 4 in $4s^1$ indicates that potassium is in Period 4. The notation s^1 means that potassium has one valence electron that is in an s orbital. Therefore, potassium must be in the s block.

Check Your Solution

All elements in Group 1 have electron configurations ending in the notation s^1 . The link between n value and period number is correctly applied. Potassium has an electron configuration with the general notation of ns^1 , which is characteristic of s block elements.

Practice Problems

11. Write complete and condensed electron configurations for yttrium, Y.
12. Write complete and condensed electron configurations for lead, Pb.
13. What elements have the valence electron configuration that is given by ns^2 ?
14. What elements have the valence electron configuration that is given by $ns^2(n-1)d^3$?

15. What are the two exceptions to the guidelines for filling orbitals in Period 4? Draw the partial orbital diagrams you would expect for them, based on the aufbau principle. Then draw partial orbital diagrams that represent their actual electron configurations. Finally, explain why the discrepancy arises.
16. The condensed electron configuration for strontium is $[\text{Kr}]5s^2$. Without using a periodic table, identify the group number to which strontium belongs. Show your reasoning.
17. Identify the following elements and write condensed electron configurations for atoms of each element.
- The d -block element in Period 4 with 10 valence electrons.
 - The element in Period 6 with 3 valence electrons.
18. The condensed electron configuration for titanium is $[\text{Ar}]4s^23d^2$. Without a periodic table, identify the period number to which titanium belongs. Show your reasoning.
19. The condensed electron configuration for arsenic is $[\text{Ar}]4s^23d^{10}4p^3$. Without using a periodic table, identify the orbital block in the periodic table to which arsenic belongs. Show your reasoning.
20. Without a periodic table, and based on the condensed electron configuration given below, identify the group number, period number, and orbital block to which each of the following elements belongs. Show your reasoning.
- francium, $[\text{Rn}]7s^1$
 - tungsten, $[\text{Xe}]6s^24f^{14}5d^4$
 - antimony, $[\text{Kr}]5s^24d^{10}5p^3$

Electron Configurations and Periodic Trends in Atomic Properties

Periodic trends involve properties such as atomic radius, ionization energy, metallic character, and electron affinity. These trends are related to patterns in electron configurations.

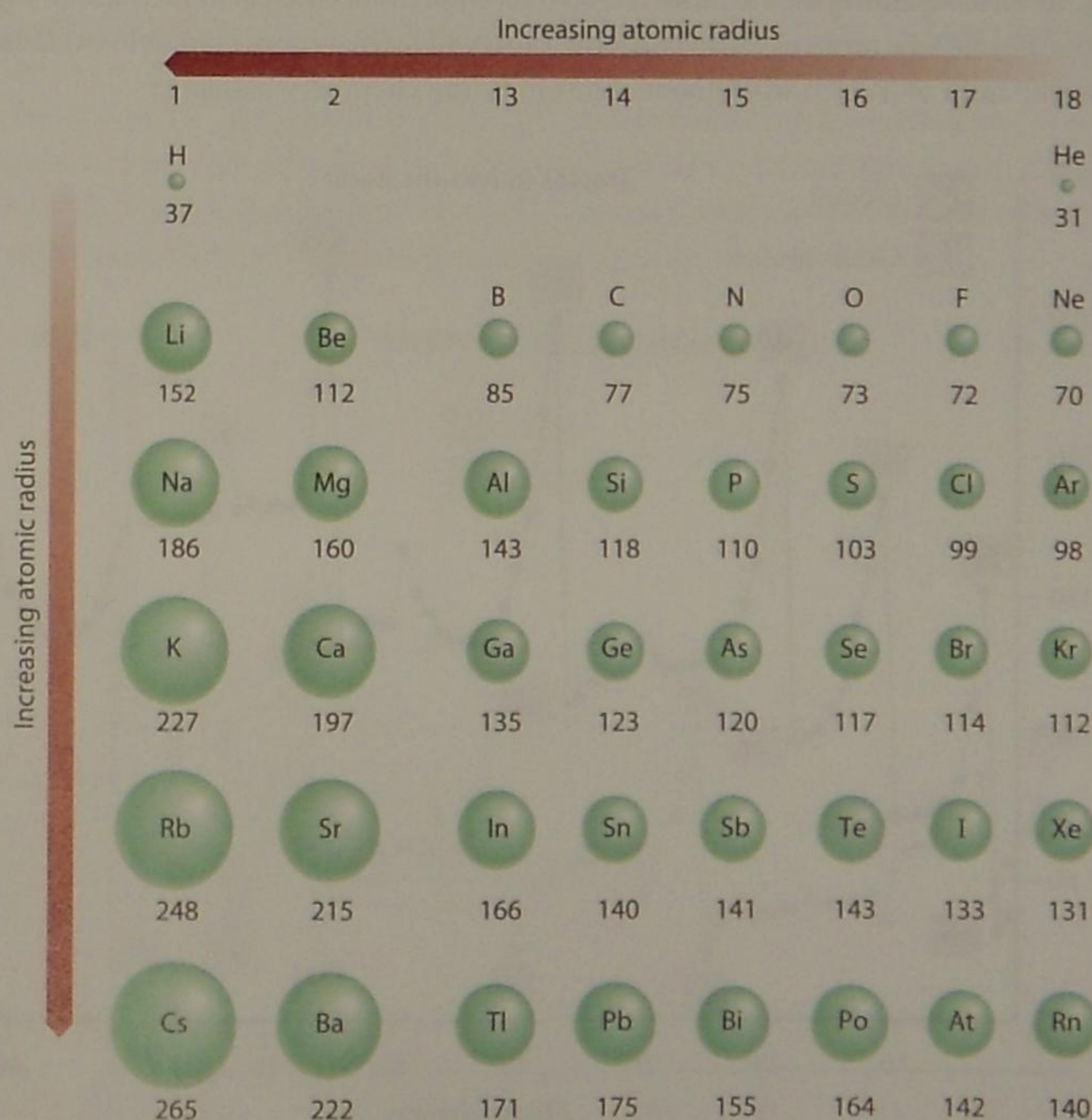
Atomic Radii

Chemists can determine the size of an atom—its **atomic radius**—by measuring the distance between the nuclei. For metals, the atomic radius is half the distance between neighbouring nuclei in a crystal. For elements that commonly occur as molecules, the atomic radius is half the distance between nuclei of identical atoms that are chemically bonded together.

Figure 3.21 shows the measured values of atomic radii for main-group elements.

Suggested Investigation

ThoughtLab Investigation
3-C, Extending the
Periodic Table



atomic radius half the distance between the nuclei of two adjacent atoms; for metals, between atoms in a crystal, and for molecules, between atoms chemically bonded together

Figure 3.21 Atomic radii of the main-group elements generally decrease across a period, and increase down a group. This general trend applies to the entire periodic table. Values for atomic radii are given in picometres (pm), which is equivalent to 1×10^{-12} m.

Factors Affecting Atomic Radii

Two factors affect differences in atomic radii.

1. As n increases, there is a higher probability of finding electrons farther from their nucleus. Therefore, the atomic volume is larger. In other words, the atomic radius tends to increase with increasing n , and it tends to decrease with decreasing n .
2. Effective nuclear charge determines the *net* force of attraction between electrons and the nucleus. Only hydrogen's lone electron experiences the full charge of its nucleus, so the nuclear charge experienced by the electron in hydrogen is Z , its atomic number. For all other atoms, the nuclear charge that any given electron experiences is somewhat reduced by other electrons that are closer to the nucleus. Thus, the net force of attraction—the effective nuclear charge, Z_{eff} —is somewhat less than Z . As Z_{eff} increases, electrons are attracted more strongly, so the size of the atom decreases. As Z_{eff} decreases, there is a reduced force of attraction, and the size of the atom increases. Valence electrons, especially, experience a smaller Z_{eff} than inner electrons, because the inner electrons shield them from the attractive force of the nucleus.

For the main-group elements, the combined influences of n , Z_{eff} , and this shielding effect have the outcomes listed below and summarized in **Figure 3.22**.

- n governs the trend of increasing atomic radius down a group. Down a group, atoms of each subsequent element have one more level of inner electrons, increasing the shielding effect. The increase in atomic size, therefore, results from the increasing value of n .
- Z_{eff} governs the trend of decreasing atomic radius across a period. Across a period, atoms of each element have one more electron added to the same outer energy level— n does not change. However, one more proton increases the Z_{eff} , which pulls the electrons closer to the nucleus. The decrease in atomic size across a period, therefore, results from increasing Z_{eff} . A higher Z_{eff} means the electrons are more strongly attracted to the nucleus and so the atomic size of the atoms decreases as you move across a period.

Atoms of transition elements do not display the same general trend as the main-group elements, because shielding by the inner d electrons counteracts the usual increase in Z_{eff} . As a result, the atomic size remains fairly constant. (You will learn a more complete explanation for the atomic radii of transition-element atoms in future chemistry courses.)

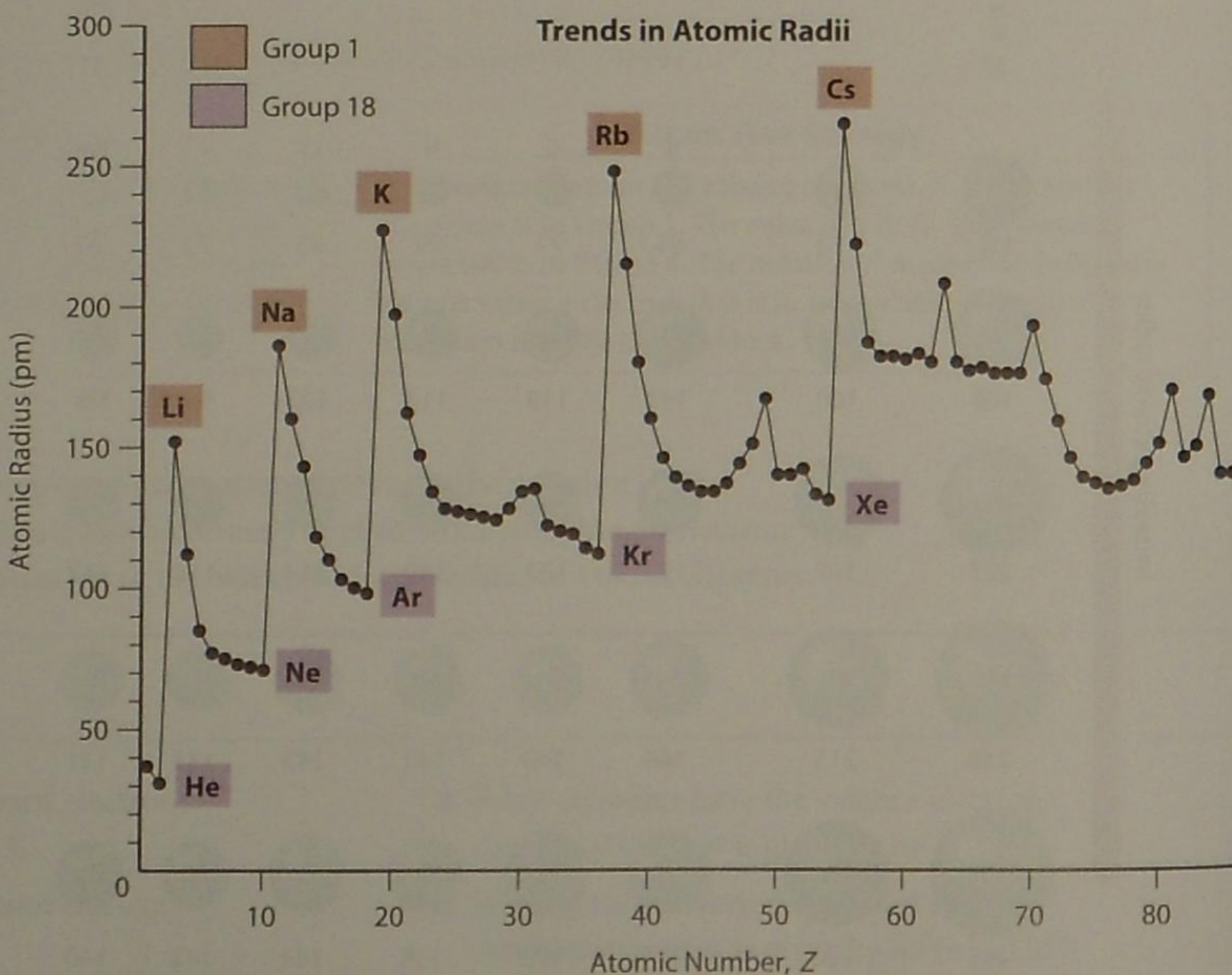


Figure 3.22 A plot of atomic radius vs. atomic number for elements of Periods 1 to 6 shows that the radius generally decreases through a period to the noble gas and then increases suddenly to the next alkali metal. Deviation from this trend occurs among the transition metals.

Ionization Energy

The formation of a positive ion (cation) requires the removal of an electron from a neutral atom. The energy needed to completely remove one electron from a ground-state gaseous atom is called the **ionization energy**. In order to remove an electron from an atom, energy is needed to overcome the force of attraction that is exerted on the electron by the nucleus. Therefore, in multi-electron atoms, more than one ionization energy exists. A gaseous atom's *first ionization energy* is the least amount of energy required to remove an electron from the outermost occupied energy level. The *second ionization energy* is always greater than the first ionization energy, because the electron must be removed from a positively charged ion. The same reasoning applies for successive ionization energies.

An atom's first ionization energy (IE_1) is closely linked to its chemical reactivity. Atoms with a low IE_1 tend to form cations during chemical reactions. **Figure 3.23** shows that the atoms with the lowest IE_1 are those belonging to Group 1 elements. These elements are among the most reactive elements in the periodic table. Atoms of elements with high IE_1 tend to form negatively charged ions (anions). The exception is the noble gases, which do not form ions naturally.

Figure 3.23 shows the overall periodic trends associated with ionization energy. Within a group, first ionization energies generally decrease as you move down the group. This trend is the inverse of the trend for atomic radius. The two trends are, in fact, linked. As the atomic radius increases, the distance of valence electrons from the nucleus also increases, so the force of attraction exerted by the nucleus on valence electrons decreases. As a result, less energy is needed to remove one such electron.

Within a period, first ionization energies generally increase from left to right. This trend is also linked to the atomic radius. Across a period, the atomic radius decreases because Z_{eff} increases. The increased effective nuclear charge of each successive element increases the attractive forces between the nucleus and valence electrons. Therefore, more energy is needed to remove one such electron.

There are several variations in the periodic trends associated with first ionization energies. These include boron and aluminum in Group 13 and oxygen and sulfur in Group 16. The observed drops in IE_1 can be explained in terms of the electron configurations for these atoms. Recall that atoms are most stable when orbitals are half-filled or completely filled. For B ($[\text{He}]2s^22p^1$) and Al ($[\text{Ne}]3s^23p^1$), removal of the only p orbital electron in each will produce more stable filled-orbital electron configurations for these atoms. For O ($[\text{He}]2s^22p^4$) and S ($[\text{Ne}]3s^23p^4$), removal of one p orbital electron in each will produce more stable half-filled orbital electron configurations for these atoms.

ionization energy the energy required to remove an electron from a ground-state atom in the gaseous state

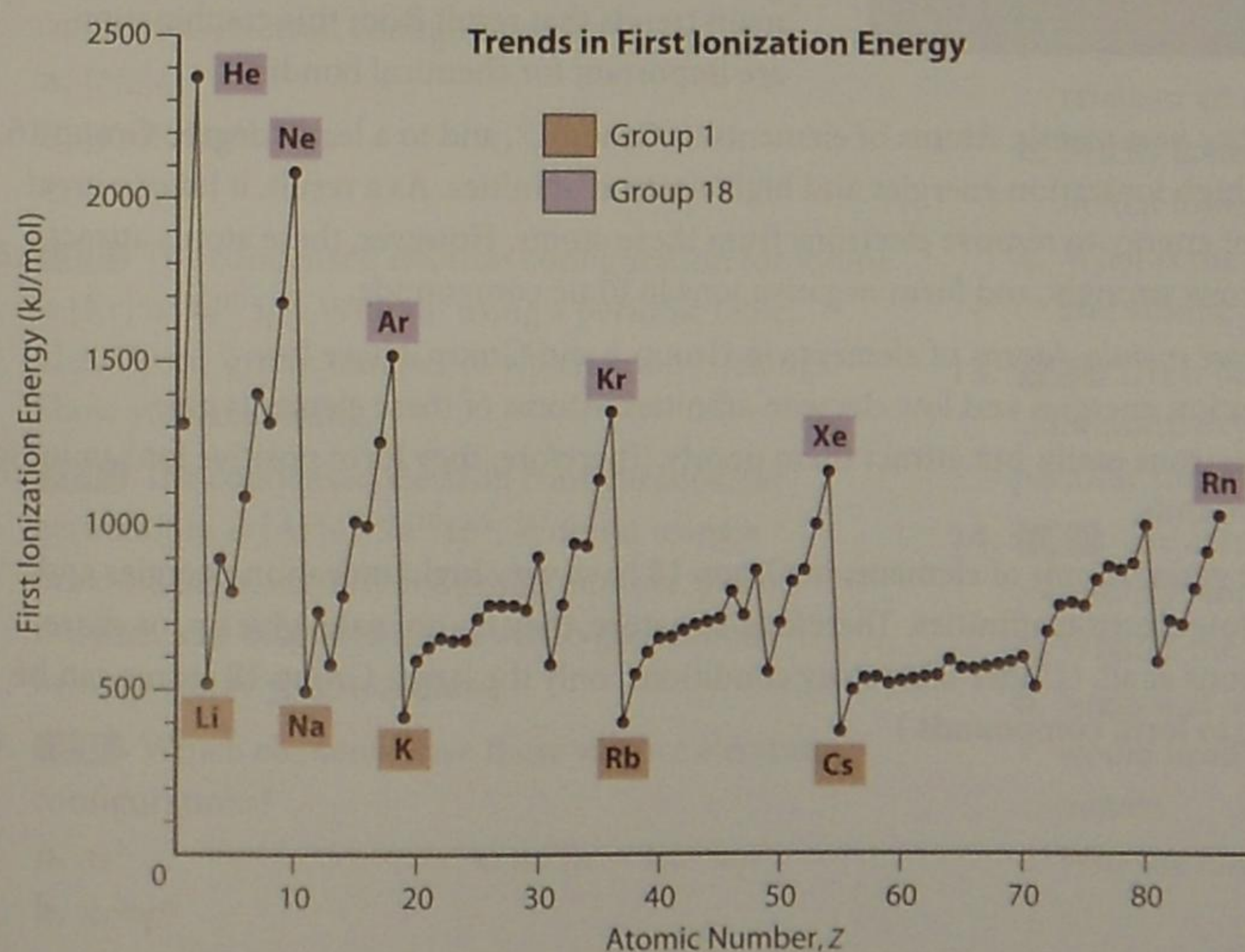


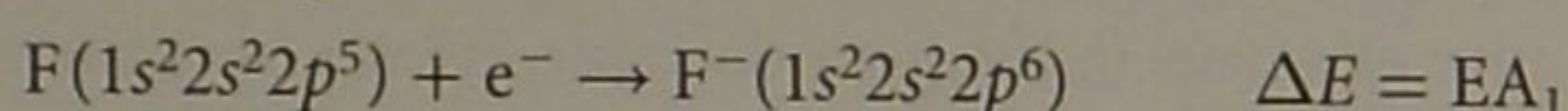
Figure 3.23 A plot of first ionization energy vs. atomic number for elements of Periods 1 to 6 shows that the lowest values occur for the alkali metals and the highest for the noble gases. This trend is the inverse of the trend in atomic size.

Reactivity of Metals

Periodic trends in ionization energy are linked to trends involving the reactivity of metals. Metals tend to readily lose electrons during chemical reactions, compared with non-metals. This is because of the low ionization energies of metals. In general, the chemical reactivity of metals increases down a group and increases from right to left across a period.

Electron Affinity

The energy change (in kJ/mol) that accompanies the addition of 1 mol of electrons to 1 mol of gaseous atoms or ions is known as **electron affinity**. As with ionization energy, there is a first electron affinity, a second electron affinity, and so on. The *first electron affinity* (EA_1) results in the formation of a gaseous anion with a charge of $1-$. For example, when a neutral fluorine atom acquires an electron, the resulting electron configuration of the fluoride ion is the same as that of the noble gas, neon:



Fluorine is very reactive, and the relative ease with which it gains an electron when it forms bonds is reflected in its high electron affinity. In most cases, energy is released

when the first electron is added, because it is attracted to the atom's nuclear charge. Thus, EA_1 is usually negative. The second electron affinity (EA_2), on the other hand, is always positive, because energy must be absorbed in order to overcome electrostatic repulsions and add another electron to a negative ion. Large negative numbers mean a high electron affinity. Small negative numbers and positive numbers mean a low electron affinity. Some representative first electron affinities are shown in **Figure 3.24**.

Trends for electron affinity are more irregular than those for atomic radius and ionization energy, because factors other than atomic size and Z_{eff} are involved. In future chemistry courses, you will learn about these factors and how they explain the irregularities. However, the property of electron affinity is still significant when considered in combination with ionization energy. Three main trends that result from this combination are important for chemical bonding.

1		Electron Affinities						8
H								He (0.0)
-72.8	2	B	C	N	O	F		Ne (+29)
-59.6	Be ≤0	-26.7	-122	+7	-141	-328		
Na	Mg	Al	Si	P	S	Cl	Ar	
-52.9	≤0	-42.5	-134	-72.0	-200	-349	(+35)	
K	Ca	Ga	Ge	As	Se	Br	Kr	
-48.4	-2.37	-28.9	-119	-78.2	-195	-325	(+39)	
Rb	Sr	In	Sn	Sb	Te	I	Xe	
-46.9	-5.03	-28.9	-107	-103	-190	-295	(+41)	
Cs	Ba	Tl	Pb	Bi	Po	At	Rn	
-45.5	-13.95	-19.3	-35.1	-91.3	-183	-270	(+41)	

Figure 3.24 This table of some representative first electron affinities shows the very large negative values for the Group 17 elements.

1. *Reactive non-metals.* Atoms of elements in Group 17, and to a lesser degree Group 16, have high ionization energies and high electron affinities. As a result, it takes a great deal of energy to remove electrons from these atoms. However, these atoms attract electrons strongly, and form negative ions in ionic compounds.
2. *Reactive metals.* Atoms of elements in Group 1 and Group 2 have low ionization energies and low electron affinities. Atoms of these elements give up electrons easily, but attract them poorly. Therefore, they form positive ions in ionic compounds.
3. *Noble gases.* Atoms of elements in Group 18 have very high ionization energies and very low electron affinities. Therefore, in nature, they do not gain, give up, or share electrons at all. (Under laboratory conditions, only the larger Group 18 atoms can be made to form compounds.)

Section 3.3 Review

Section Summary

- For hydrogen, the relative energies of the atomic orbitals depend only on the principal quantum number, n . For many-electron atoms, other factors such as the orbital-shape quantum number, l , influence the relative energies of atomic orbitals.
- Electron configuration notation and orbital diagrams are two methods commonly used to represent or describe the distribution of electrons in atoms.
- Applying the Pauli exclusion principle, Hund's rule, and the aufbau principle, the electron configuration of atoms can be built up according to the position of the element in the periodic table.
- The modern, quantum mechanical model of the atom enables us to understand the elements, their positions in the periodic table, and their chemical and physical properties based on their electron configuration.

Review Questions

1. **K/U** Refer to Table 3.5. Draw a table that shows the quantum numbers, electron configuration, and orbital diagram for the electrons in nitrogen.
2. **K/U** A carbon atom has two electrons total in its $2p$ orbitals. If one of these electrons has an electron spin number of $+\frac{1}{2}$, what is the electron spin number of the other electron? Explain your answer in terms of Hund's rule.
3. **T/I** Examine the following orbital diagram for a neutral atom in its ground state.

$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow
$1s$	$2s$	$2p$		

 - a. What element is represented here? How do you know?
 - b. Explain how Hund's rule applies to this orbital diagram.
 - c. Explain how the Pauli exclusion principle applies to this orbital diagram.
4. **T/I** What is wrong with each of the following condensed electron configurations?
 - a. $[\text{Ne}]4s^2$
 - b. $[\text{Kr}]5s^25p^6$
 - c. $[\text{Br}]5s^2$
5. **T/I** The condensed electron configuration for iodine is $[\text{Kr}]5s^24d^{10}5p^5$. Without using a periodic table, identify the group number to which iodine belongs. Show your reasoning.
6. **T/I** The condensed electron configuration for germanium is $[\text{Ar}]4s^23d^{10}4p^2$. Without using a periodic table, identify the group number, period number, and orbital block to which germanium belongs. Show your reasoning.
7. **K/U** Which elements have these valence electron configurations?
 - a. ns^1
 - b. ns^2np^6
 - c. $ns^2(n-1)d^{10}np^4$
8. **T/I** Use Pauli exclusion principle, Hund's rule, and the aufbau principle to write condensed electron configurations for atoms of the following elements:
 - a. potassium, K
 - b. selenium, Se
 - c. xenon, Xe
9. **K/U** The ns orbitals usually fill before the $(n-1)d$ orbitals. Why are there exceptions to this rule?
10. **T/I** Referring only to the periodic table at the back of your textbook, arrange the following sets of elements in order of increasing atomic radius. Briefly explain your reasoning.
 - a. Be, Ca, Ba
 - b. Na, Al, Cl
 - c. Li, Rb, Sn
11. **C** Your friend Zen is studying for tomorrow's chemistry test and texts you to ask about the difference between Z and Z_{eff} . Write a text to explain, being as brief as possible while including all important information.
12. **K/U** First ionization energy is an important atomic property.
 - a. What is first ionization energy and how does it relate to an atom's chemical reactivity?
 - b. Briefly summarize and explain the periodic trends in first ionization energy.
 - c. What is the relationship between ionization energy and atomic radius?
13. **C** Draw diagrams to illustrate why boron, aluminum, oxygen, and sulfur deviate from the periodic trends in ionization energy.
14. **A** The extremely reactive Group 1 metals are commonly stored in oil.
 - a. What is the purpose of the oil?
 - b. Suggest at least one safety precaution a chemist would need to take when working with Group 1 metals.
 - c. Why are Group 1 metals so reactive?

CANADIAN RESEARCH IN ACTION

Enhanced MRI Images and Epilepsy Research



Dr. Jorge Burneo (centre) and his colleagues Dr. Rob Bartha (on the right) and Jake Penner (doctoral candidate, on the left) are shown here with the 7 Tesla MRI that they use in their research into epilepsy.

Four to five of every one thousand Canadians have epilepsy, a disorder characterized by sudden changes in brain function that often result in seizures. Thirty percent of individuals with epilepsy do not respond to medications and are diagnosed with *medically-intractable epilepsy*. Dr. Jorge Burneo of the University of Western Ontario in London, Ontario hopes to better understand the causes of this condition with the help of the newest addition to the university's research arsenal, a 7 Tesla MRI. MRI (magnetic resonance imaging) technology uses radio waves along with a powerful magnet and a computer to generate images of soft tissue. Like electrons, protons spin on their axes. However, the orientation of these axes is random. The strong magnetic field generated by the MRI magnet affects the protons in hydrogen atoms in body tissue, causing their axes to align with the same orientation. This is similar to how the needles in compasses adopt a north-south alignment when exposed to Earth's magnetic field. When exposed to radio waves at a specific frequency, certain protons are momentarily "knocked" out of this alignment. When the radio signal is removed, these protons re-align with the magnetic field, emitting their own radio waves as they do so. These signals are "read" by the computer to produce a detailed image of the body tissue. Image resolution depends on the strength of the magnet, which is measured in teslas, the SI unit of measurement for the concentration of a magnetic field. Used only for research purposes, the 7 Tesla is the world's most powerful MRI and the only one of its kind in Canada.

The 7 Tesla gives Dr. Burneo and his research team a glimpse into the brains of individuals with medically-intractable epilepsy in a way that less-powerful MRIs cannot. "We hope," Dr. Burneo states, "that with the use of the 7T technology, we will be able to identify structural abnormalities not seen in standard testing." Small changes within tissue can be detected by this powerful MRI. Dr. Burneo and his team are using a technique called magnetic resonance spectroscopy (MRS) to investigate metabolic changes in regions of the brain where seizures are generated. MRS uses special software to create a profile of all metabolites, both normal and abnormal, produced in these areas. The profile enables Dr. Burneo to study abnormal metabolic changes in these regions in individuals with medically-intractable epilepsy. In the past, these studies could only be completed by inserting electroscopes through a hole in the skull, a procedure associated with significant risk. Therefore, 7 Tesla technology provides Dr. Burneo with a safe and effective way to better understand medically-intractable epilepsy and, ultimately, help doctors treat this condition.

Related Career

MRI technicians are medical professionals who operate MRI machinery in hospitals or diagnostic imaging centres. MRI technicians undergo a two-year certification program that provides them with an understanding of MRI technology as well as a solid background in anatomy and physiology. In addition to strong technical skills, MRI technicians require skills in problem solving, communication, and team collaboration, as they work with other members of a diagnostic health-care team to provide patient care.

QUESTIONS

1. Explain the role that proton spin plays in magnetic resonance imaging.
2. During an MRI, when the radio signal is removed and the hydrogen protons re-align with the magnetic field, they emit their own radio waves. Suggest why this might occur.
3. Use Internet and/or print resources to find another career related to the research covered in this feature. Briefly describe the nature of this career and any required training or education.

Skill Check

Initiating and Planning

Performing and Recording

✓ Analyzing and Interpreting

✓ Communicating Results

Safety Precautions



- A very high voltage is required to operate the gas discharge tubes. Do not come into contact with the source while viewing the tubes.
- Do not work with the gas discharge tubes yourself. Your teacher will demonstrate them.

Materials

- spectroscope or diffraction grating
- incandescent bulb
- gas discharge tubes

Observing Spectra

(Teacher Demonstration)

When a high voltage current is passed through a glass tube that contains hydrogen gas at low pressure, the gas glows with a pinkish-purple colour. In this investigation, you will observe this gas discharge tube through a spectroscope or a diffraction grating to observe the line (emission) spectrum of hydrogen.

Pre-Lab Questions

1. Which part of the electromagnetic spectrum is visible to the human eye, and what range of wavelengths does it span?
2. Compare and contrast a continuous spectrum with a line spectrum.

Question

How can line spectra be used to identify specific elements?

Procedure

1. Practise using the spectroscope with an incandescent bulb. Point the slit toward the bulb; move the spectroscope until the spectrum is clearly visible.
2. Record the appearance of the spectrum from the incandescent bulb.
3. Your teacher will demonstrate the discharge tube apparatus for hydrogen.
4. Observe the hydrogen discharge tube, and note its colour when high-voltage current is applied to it.
5. With the lights dimmed, examine the hydrogen line spectrum with a spectroscope or diffraction grating. Make a sketch to record your observations.
6. Repeat steps 4 and 5 for the line spectra of other discharge tubes, if available.

Analyze and Interpret

1. Compare the spectrum of the incandescent bulb and the hydrogen discharge tube. If you observed other discharge tubes, compare their spectra with the spectrum from the hydrogen discharge tube.

Conclude and Communicate

2. Explain how spectra can be used to identify the presence of specific elements in a sample of a substance.

Extend Further

3. **INQUIRY** A fluorescent bulb is a type of gas discharge tube. However, the emissions of the gas are absorbed by a coating on the inside of the bulb; the excited atoms of the coating emit light when they return to their ground state. Predict what the line spectrum of a fluorescent light would look like. If you are not able to test your prediction, do research to verify it.
4. **RESEARCH** What is an atomic absorption spectrophotometer; for what it is used?

Skill Check

Initiating and Planning

- ✓ Performing and Recording
- ✓ Analyzing and Interpreting
- ✓ Communicating Results

Materials

- periodic table in Appendix B

Electronic Structures for Period 3 Elements

In this investigation, you will use the Pauli exclusion principle, Hund's rule, and the aufbau principle to represent Period 3 elements of the periodic table.

Pre-Lab Questions

1. Explain, using an example, the Pauli exclusion principle.
2. Explain, using an example, Hund's rule.
3. Explain, using an example, the aufbau principle.

Question

How can you use the Pauli exclusion principle, Hund's rule, and the aufbau principle to represent elements of the periodic table?

Procedure

1. Use the periodic table in Appendix B to answer the following questions.

Analyze and Interpret

1. Write electron configurations and orbital diagrams for atoms of sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and argon.
2. Make a table with eight columns and two rows. In the first row, write the symbol, atomic number, and condensed electron configurations for the Period 2 elements.
3. Fill in the second row with the atomic number, atomic symbol, and electron configuration for the elements in question 1.

Conclude and Communicate

4. Describe two generalizations about the table that you created.
5. For atoms of any Group 1 element, a general electron configuration is ns^1 , where n is the quantum number for the outermost occupied energy level. Use your answer to question 2 to predict general electron configurations for atoms in the following groups:
 - a. 2
 - b. 13
 - c. 14
 - d. 15
 - e. 16
 - g. 17
 - h. 18

Skill Check

Initiating and Planning

- ✓ Performing and Recording
- ✓ Analyzing and Interpreting
- ✓ Communicating

Extending the Periodic Table

Pekka Pyykkö at the University of Helsinki has predicted the position of elements up to 172. In this investigation, you will make predictions about the electron configurations of these large elements.

Pre-Lab Questions

1. List the order in which sublevels are filled in element 118.
2. If g is the next sublevel after f , what are the next three sublevels to be filled after $7p$ if the relative energies of atomic orbitals is $6d < 7p < 5g < 6f < 7d < 8p$.

Question

How should 172 elements be arranged in the periodic table?

Organize the Data

1. Complete shorthand electron configurations for elements 118 to 172.
2. Arrange these elements into groups so that they can be placed into the current periodic table. What criteria will you use?
3. Place these groups into the current periodic table. Redraw your table that now includes all 172 elements.

Analyze and Interpret

1. Describe the changes in the length of the periods and groups in each of the s , p , d , and f blocks of the periodic table.
2. Describe the properties of the elements in the groups that you arranged in step 2. Are you able to predict the properties of all of the groups? Explain.
3. Compare your periodic table (step 3) with that of your classmates. Which is best for accurately predicting the properties of the undiscovered elements?

Conclude and Communicate

4. Summarize the concepts about electron configurations of larger elements and the changes needed to accommodate 172 elements in the periodic table.
5. Experts cannot agree where the large elements beyond element 118 should go in the periodic table. What are the problems with arranging these elements?

Extend Further

6. **INQUIRY** Would a single periodic table with 172 elements be better for enabling chemists to make predictions about new elements? Explain.
7. **RESEARCH** How have Canadian scientists and/or scientists in Canadian laboratories advanced knowledge about the synthesis of new elements?

Section 3.1

The Nuclear Model of the Atom

Building on and extending from the work of scientists who came before them as well as their peers, Ernest Rutherford and Niels Bohr developed atomic models that, today, are referred to as nuclear and planetary models of the atom.

Key Terms

electromagnetic radiation	nuclear model
emission spectrum or line spectrum	photon
frequency	quantum

Key Concepts

- Historically, the development of and modifications to the atomic model have been the result of experimental evidence and new ideas about the nature of matter and energy.

- Thomson's discovery of the electron disproved Dalton's model of the atom as a solid, indivisible sphere. Instead, Thomson proposed that the atom existed as a positively charged sphere, with enough negatively charged electrons embedded in it to balance the overall charge on the atom.
- Observations and inferences made by Rutherford led to a nuclear model of the hydrogen atom. This model is still the most commonly depicted, with negatively charged electrons orbiting around a central positively charged nucleus.
- Bohr's model of the atom refined the Rutherford model, incorporating the concept that, like light, electrons in atoms could have only certain amounts of energy and, therefore, could exist in only specific orbits around the nucleus. Each allowed orbit had a specific amount of energy and a specific radius.

Section 3.2

The Quantum Mechanical Model of the Atom

New ideas and experimental evidence about the wave nature of particles led to a new, revolutionary atomic model—the quantum mechanical model of the atom.

Key Terms

atomic orbital	quantum mechanical model of the atom
magnetic quantum number, m_l	quantum numbers
orbital-shape quantum number, l	shell
principal quantum number, n	spin quantum number, m_s
Pauli exclusion principle	sublevel

Key Concepts

- According to the quantum mechanical model of the atom, electrons have both matter-like and wave-like properties.
- The position and momentum of atoms cannot both be determined with certainty, so the position is described in terms of probabilities.
- An orbital represents a mathematical description of the region of space in which an electron has a high probability of being found.
- The first three quantum numbers describe the size, energy, shape, and orientation of an orbital. The fourth quantum number describes the orientation of the axis around which the electron is spinning.

Section 3.3

Electron Configurations and the Periodic Table

The quantum mechanical model of the atom explains the experimentally determined, electronic structure of the periodic table and the properties of its elements.

Key Terms

atomic radius	ionization energy
aufbau principle	Hund's rule
electron affinity	orbital diagram
electron configuration	

Key Concepts

- For hydrogen, the relative energies of the atomic orbitals depend only on the principal quantum number, n . For many-electron atoms, other factors such as the orbital-shape quantum number, l , influence the relative energies of atomic orbitals.

- Electron configuration notation and orbital diagrams are two methods commonly used to represent or describe the distribution of electrons in atoms.
- Applying the Pauli exclusion principle, Hund's rule, and the aufbau principle, the electron configuration of atoms can be built up according to the position of the element in the periodic table.
- The modern, quantum mechanical model of the atom enables us to understand the elements, their positions in the periodic table, and their chemical and physical properties based on their electron configuration.

Knowledge and Understanding

Select the letter of the best answer below.

- Which of the following best describes Rutherford's atomic model?
 - indivisible (nothing smaller than the atom exists)
 - has a very small nuclear core
 - contains protons
 - uses quantum physics to explain electron properties
 - All of these are correct.
- Which observation in the cathode ray tube experiments did not contribute to the conclusion that the electron is found in atoms of all matter?
 - The beam travelled in straight lines.
 - Changing the gases inside the cathode ray tube did not alter the path of the beam.
 - Changing the metals of the electrodes did not change the path of the beam.
 - Two of these are correct.
 - All of these are correct.
- The history of science records the discoveries and achievements of various scientists whose models of the atom helped to develop and further our understanding of the nature and behaviour of matter. Choose the correct historical sequence of atomic models from the following choices.
 - Dalton, Rutherford, Thomson, Bohr
 - Thomson, Rutherford, Bohr, Dalton
 - Dalton, Thomson, Rutherford, Bohr
 - Dalton, Bohr, Rutherford, quantum
 - Dalton, Bohr, Thomson, quantum
- The emission spectrum of an element
 - has a dark background with bright-coloured lines.
 - has a rainbow-coloured background with dark lines.
 - has lines that represent the location of electrons inside the atom.
 - has spaces between the lines that represent the distance between electrons inside the atom.
 - is a continuous spectrum of visible light.
- Which one of the following electron configurations represents an electron in an excited state?
 - $[\text{Ar}]4s^23d^{10}4p^3$
 - $[\text{Ar}]4s^23d^{10}4p^6$
 - $[\text{Ar}]4s^23d^{10}4p^2$
 - $[\text{Ar}]4s^23d^{10}4p^4$
 - $[\text{Ar}]4s^23d^{10}4p^35s^1$
- Which of the following elements could have the following valence orbital diagram?

s
 p

 - carbon
 - nitrogen
 - boron
 - sulfur
 - neon
- First ionization energy is
 - the amount of energy an electron must gain to escape from a neutral atom.
 - the amount of energy an electron must lose to escape from a neutral atom.
 - the amount of energy an atom gains when it first becomes an ion.
 - Two of these are correct.
 - All of these are correct.
- Electron affinity refers to
 - the energy change accompanying the addition of 1 mol of gaseous atoms or ions.
 - the attraction of the nucleus for electrons.
 - the attraction of electrons for one another.
 - the energy change of electrons of noble gas elements.
 - none of the above.
- In which period can you start to use condensed electron configurations?
 - 1
 - 2
 - 3
 - 4
 - 5
- Atomic radius decreases
 - when the effective nuclear charge decreases.
 - when the inner core decreases.
 - down a group.
 - across a period.
 - in all of the above situations.
- Which property changes in the same way that the atomic radius does in the periodic table?
 - electron affinity
 - atomic number
 - ionization energy
 - They all change in the same way.
 - None of them change in the same way.

12. Which two sets of quantum numbers describe electrons in the same sublevel?

- a. i, ii
- b. iii, v
- c. ii, iii
- d. iv, v
- e. ii, iv

	n	l	m_l	m_s
i.	2	1	0	$-\frac{1}{2}$
ii.	2	1	-1	$+\frac{1}{2}$
iii.	3	1	-1	$+\frac{1}{2}$
iv.	2	2	-1	$+\frac{1}{2}$
v.	3	2	-1	$+\frac{1}{2}$

13. When comparing the properties of carbon atoms and oxygen atoms, which statement is correct?

- a. Carbon and oxygen have the same spin quantum number, m_s .
- b. Carbon and oxygen have the same magnetic quantum number, m_l .
- c. Carbon and oxygen have the same principal quantum number, n .
- d. Carbon has a greater orbital-shape quantum number, l , than oxygen.
- e. Oxygen has a greater orbital-shape quantum number, l , than carbon.

14. Helium behaves like a noble gas because

- a. its valence shell is completely filled.
- b. its outermost orbital is completely filled.
- c. its outermost energy level is completely filled.
- d. Two of these are correct.
- e. All of these are correct.

Answer the questions below.

15. In what ways were Dalton's and Thomson's atomic models similar? In what ways were they different?

16. In what ways were Thomson's and Rutherford's models of the atom similar? In what ways were they different?

17. What is common to all atomic models, from Dalton's to Bohr's?

18. What property is common to all electromagnetic radiation?

19. Describe how the motion of an electron in Bohr's model of the atom is different from the motion of an electron in the quantum mechanical model of the atom.

20. Bohr's atomic model provides specific information about the energy and location of electrons in an atom. That is, the model predicts that both of these can be known with certainty. What structures (such as the nucleus) in the Bohr model are necessary to allow for these concepts?

21. Explain how periodic trends in ionization energy and electron affinity explain why atoms of elements in Group 1 and Group 2 tend to bond with other elements by forming positive ions in ionic compounds.

22. A nitrogen atom has a total of three electrons in its $2p$ orbitals. Are any of these electrons paired? Explain how you know.

23. The quantum mechanical model provides information about the atom that is certain and uncertain. Which information is certain? Which is uncertain?

24. What information do the quantum numbers provide about an orbital?

25. What two things does the principal quantum number, n , describe about an orbital and the electron in it?

26. Why does it make sense that an electron can be found farther away from the nucleus in an orbital of a higher energy level than in the same type of orbital in a lower energy level?

27. What is the Pauli exclusion principle, and how is it related to the spin quantum number, m_s ?

28. What is Hund's rule and its significance?

29. Why does it make sense that electron configurations represent atoms in their ground state and not their many excited states?

30. What are the general trends for atomic radius down a group and across a period in the periodic table? Account for these trends.

Thinking and Investigation

31. If it had turned out that the cathode beam particle had a neutral charge, which experimental finding(s) would have remained the same in all of the cathode ray tube experiments?

32. Without consulting a periodic table, determine to which period, group, and block the element with the electron configuration $[\text{Xe}]6s^25d^{10}$ would belong.

33. Write the complete electron configuration for the element in Period 5 and Group 15.
34. List the $3s$, $5s$, $2p$, $4p$, $3d$, and $5d$ orbitals in order, from the lowest energy to the highest energy.
35. List all possible values of m_l for electrons in the element having the electron configuration $[\text{Ar}]4s^23d^5$.
36. Use a basic periodic table, which does not contain electron configurations, to determine which element is defined by $[\text{Ar}]4s^23d^8$.
37. Use a basic periodic table, which does not contain electron configurations, to determine which element is defined by $[\text{Ne}]2s^22p^1$.
38. Use a basic periodic table, which does not contain electron configurations, to determine which element is defined by $[\text{Kr}]5s^24d^{10}5p^4$.
39. If the last electron to be added to an atom was the seventh electron in the third energy level, what element would that be?
40. If the last electron to be added to an atom was the 44th electron in the atom, what element would that be?
41. If the last electron to be added to an atom was the sixth electron in the second energy level, what element would that be?
42. If the last electron to be added to an atom was the second electron in the sixth energy level, what element would that be?
43. Some chemists do not include the d electrons in the condensed electron configurations for large p -block elements. For example, they would write the condensed electron configuration for tin as $[\text{Kr}]5s^22p^2$. Why do you think this might be a valid way of writing the electron configurations?
44. Use Z_{eff} to predict which atom should be larger between boron and fluorine.
45. Use Z_{eff} to predict which atom should be larger between magnesium and silicon.
46. Use Z_{eff} to predict which atom should be larger between calcium and selenium.
47. The largest artificial element that scientists have been able to create to date has an atomic number of 118 and occupies the last available spot on the modern periodic table. Using only the organization of the periodic table, determine each of the following for element 118:
- condensed electron configuration
 - set of quantum numbers for the last electron to be added to it
 - physical state at room temperature
 - reactivity
48. **T/I** Referring only to a periodic table, arrange the following sets of elements in order of increasing first ionization energy. Briefly explain your reasoning.
- Na, Si, Ar
 - He, Li, Be
 - Mg, Ca, Ba
49. **T/I** Consider the electron configuration: $1s^22s^22p^4$.
- Assume the electron configuration represents a neutral atom in its ground state. What element does it represent? Explain how you know.
 - What information does this electron configuration notation provide?
 - What information does this electron configuration notation *not* provide?

Communication

50. **BIG IDEAS** Technological devices that are based on the principles of atomic and molecular structures can have societal benefits and costs. Ultraviolet (UV) radiation technology is used in a wide variety of applications, including disinfection, curing of polymers and resins, detection of trace chemicals, and non-invasive testing. Research one of these and create a graphic organizer that lists the benefits, costs, and potential hazards to society.
51. **BIG IDEAS** Technological devices that are based on the principles of atomic and molecular structures can have societal benefits and costs. X rays were discovered “accidentally” when closed photographic plates were exposed near cathode ray tubes that were left operating. Cathode ray tubes are used in CRT computer monitors. Research the discovery of the X ray, and in a series of small paragraphs, describe how X rays can be released in cathode ray tubes, the precautions that are taken to prevent the unguarded release of X-ray radiation from the CRT computer monitor, and any other precautions or warnings that are necessary that extend from the use of a cathode ray tube in a computer monitor.
52. Use labelled diagrams to compare the concept of an orbit with the concept of an orbital. Be as detailed as possible in your answer.
53. The concept of orbitals overlapping in three-dimensional space to create an overall spherical atom is a difficult image for many people to construct in their minds. Suggest or build a model that can help to give this image more concrete substance to help people understand it better.

54. Your friend is having a hard time understanding condensed electron configurations. Write an e-mail, giving one example of a condensed electron configuration, explaining why they are used, and helping to avoid any possible misconceptions.
55. Create a simple diagram of a main-group element that includes a nucleus, an inner core of electrons, and a valence shell. Use these terms to describe how the effective nuclear charge, Z_{eff} is determined.
56. Create a diagram or graphic organizer to summarize all of the periodic trends described in this chapter.
57. This chapter presented ideas from several scientists who made significant contributions to the quantum mechanical model of the atom. These scientists include Bohr, Planck, Heisenberg, de Broglie, and Schrödinger. Other scientists whose work was integral for this model include Albert Einstein and Paul Dirac. Use this chapter as a starting point to conduct research about the roles played by each of these scientists in developing the quantum mechanical model of the atom. Present your findings in the form of a summary table or illustrated essay.
58. Summarize your learning in this chapter using a graphic organizer. To help you, the Chapter 3 Summary lists the Key Terms and Key Concepts. Refer to Using Graphic Organizers in Appendix A to help you decide which graphic organizer to use.
61. Rutherford introduced three new structural features to the atomic model.
- Identify these three features.
 - Explain how each of these features challenged the established concepts of science at the time (late 1800s and early 1900s).
62. The success of a theory or model is judged by how well it can explain and predict experimental findings. The Bohr model was at the same time highly successful and highly unsuccessful. Explain.
63. Interview a health-care professional in your community about infrared (IR) spectroscopy and near-infrared spectroscopy (NIRS), and determine the following:
- Is it available in your area?
 - Is it commonly used?
 - Is the quality of this diagnostic application as good as other methods, such as MRIs?
 - Is the waiting period to have this diagnostic application done shorter, as long as, or longer than MRIs in your area?
64. Ultraviolet (UV) radiation is used in scanners to detect counterfeit money. Research what the special markers are that are embedded in legitimate bills that are meant to be detected by UV scanners. What is the science behind why these markers show up under the scanners?

Application

59. Most of the scientists who developed atomic models or whose work was important in the development of atomic models were not chemists but were, rather, physicists and mathematicians.
- What skills and prior knowledge do you think the physicists and mathematicians contributed to complement the skills and knowledge of chemists?
 - For what reasons do you think physicists in particular were interested in studying the atom?
60. The Thomson model of the atom is an example of a “continuum of matter,” whereas the Rutherford model of the atom is an example of “quantized matter.” Explain what you think this means.
65. The brightly coloured lights of fireworks are caused by the same principles as the emission spectra of elements. Research which elements are commonly responsible for red, green, blue, and purple in most firework displays. Use a table to summarize your findings.
66. The concepts of continuum versus quantum amounts can be challenging to understand without suitable analogies. With a classmate, brainstorm examples of continuous versus quantized versions of amounts, positions, or situations all around you. Record them in a chart like the one below.

Scenario	Example	
	Continuous Version	Quantized Version
Climbing	Using a ramp	Using a ladder or staircase
Paying an amount of money		
Getting down a snowy hill		

67. Create a new periodic table of the first 92 elements if the quantum numbers were as follows:

$$n = 1, 2, 3 \dots$$

$$l = 1, 2 \dots n - 1$$

$$m_l = -n \dots 0 \dots +n$$

$$m_s = +\frac{1}{2}, -\frac{1}{2}$$

68. Based on the periodic table you developed in the previous question, name the new noble gases.
69. Write a condensed electron configuration for an imaginary element X with atomic number 127.
70. The periodic table was originally organized into periods and groups according to the similarities and patterns of chemical behaviour that emerged by observing the known elements. Now it is apparent that the quantum mechanical model of the atom would organize the elements in a similar way. List four major patterns in the periodic table that correspond to the quantum mechanical model.
71. Lead and carbon are part of the same group on the periodic table, so they have the same number of valence electrons. However, their chemical and physical properties are dramatically different. Explain how and why this is the case.
72. Only two elements are liquids at 25°C: mercury and bromine. Chemists do not know the properties of all the elements, because some have never been prepared in quantities large enough for investigation. In these cases, chemists rely on periodic trends to predict their properties. One of the elements whose properties are predicted is francium (Fr). Its most stable isotope has a half-life of 21 min, so only traces of francium exist on Earth, and no measurable quantity has been prepared or isolated. Could francium be a liquid at 25°C? Do the following to make a prediction.
- Plot a graph of the Group 1 elements, with atomic number on the x-axis and melting point (in °C) on the y-axis. Use the following rounded values: Li, 181°C; Na, 98°C; K, 64°C; Rb, 39°C; Cs, 28°C.
 - Determine by how much the melting point drops between successive pairs of elements (e.g., from lithium to sodium, from sodium to potassium, etc.).
 - Use your graph and your answers for part (b) to infer a reasonable value for the melting point of francium.
 - Predict whether francium will be a liquid at 25°C.

73. The history of the development of the quantum mechanical model of the atom, as well as subsequent advances in the application of quantum mechanics to chemistry, tends to focus on the achievements of male scientists. Because of the pivotal roles played by male scientists, one could easily get the impression that few or no female scientists were involved. This is certainly not the case. Do research to find out the achievements of the following female scientists in the history of quantum mechanics and quantum chemistry:

- Inga Fischer-Hjalmars (1918–2008)
- Maria Goeppert-Mayer (1906–1972)
- Sigrid Peyerimhoff (1937–##)
- Alberte Pullman (1920–2011)
- Hertha Sponer (1895–1968)

In communicating your findings, include information about challenges these scientists faced as women working in their fields, as well as any information that you, personally, found interesting or surprising.



Inga Fischer-Hjalmars



Sigrid Peyerimhoff



Hertha Sponer



Maria Goeppert-Mayer



Alberte Pullman

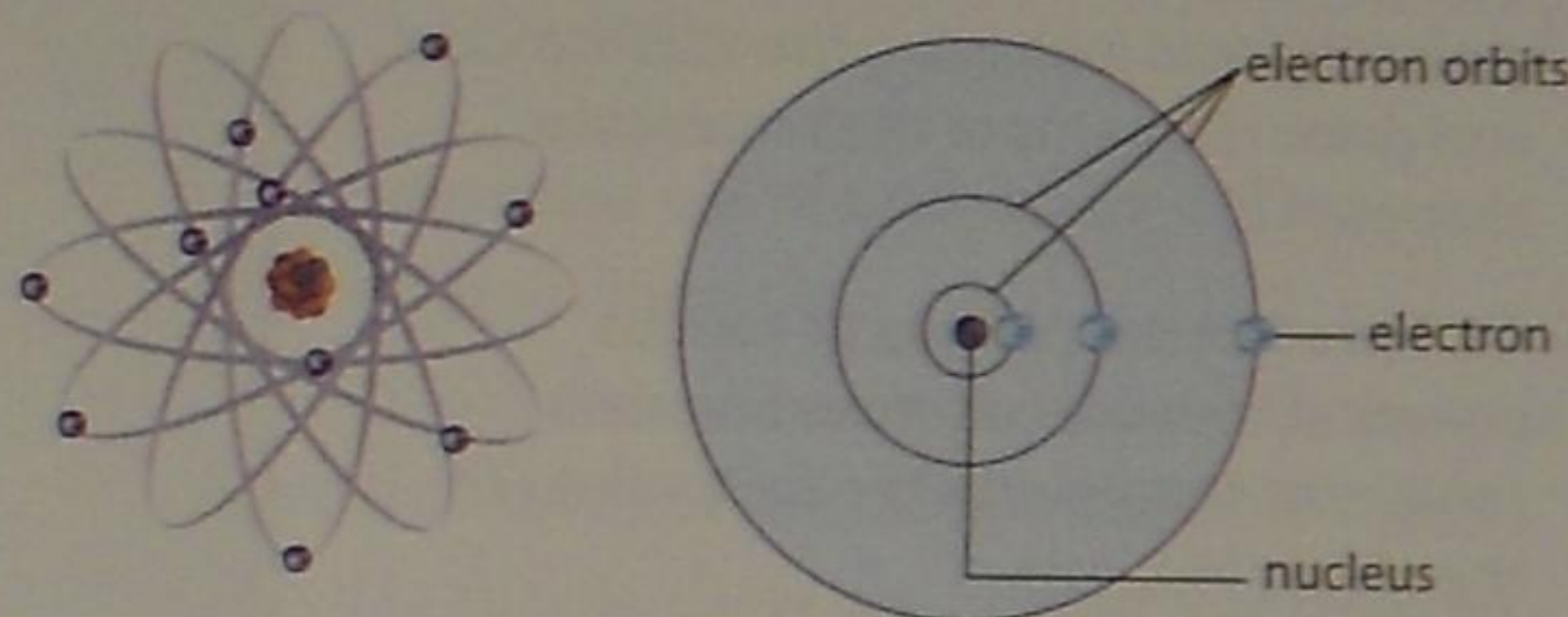
Select the letter of the best answer below.

- K/U** Which of the following did Ernest Rutherford use in his gold foil experiment that helped to establish a new model for the atom?
 - a beam of protons
 - a cathode ray beam
 - a beam of alpha particles
 - a beam of X rays
 - a beam of beta particles
- K/U** Which “feature” of atomic structure was discovered the earliest?
 - the electron
 - the proton
 - the nucleus
 - the orbit
 - empty space
- K/U** Which aspect of Rutherford’s and Bohr’s orbits was different?
 - Rutherford’s orbits were elliptical and Bohr’s were circular.
 - Electrons were in constant motion in Rutherford’s orbits but not in Bohr’s.
 - There was empty space between the orbits and the nucleus in Rutherford’s model but not in Bohr’s.
 - Electrons gave off energy in Rutherford’s orbits but not in Bohr’s.
 - Bohr’s orbits could be called orbitals because they were quantized, but Rutherford’s could not.
- K/U** As Bohr understood them, the dark spaces in the atomic spectrum of hydrogen corresponded to
 - the energy between the energy levels inside the atom.
 - the energy between the sublevels of energy within each energy level.
 - the energy of the excited electrons that did not translate into a quantum leap.
 - the space between the energy levels inside the atom; that is, where the electron could be.
 - none of the above.
- K/U** Which one of the following means the same as “orbital”?
 - orbit
 - energy level
 - shell
 - wave function
 - Two of these are correct.
- A** If the 24th electron is the last one filled in an element, which element is it?
 - chromium
 - titanium
 - manganese
 - zirconium
 - molybdenum
- T/I** Which element, in its ground state, would not have an electron with the quantum numbers $n = 3$, $l = 1$, $m_l = 0$, $m_s = +\frac{1}{2}$ in their atoms?
 - calcium
 - bromine
 - sulfur
 - tin
 - magnesium
- K/U** Which scientist is responsible for the rule that states only two electrons are allowed in one orbital?
 - Bohr
 - Schrödinger
 - Aufbau
 - Pauli
 - Hund
- K/U** Which periodic trend increases down a group and decreases across a period?
 - electron affinity
 - ionization energy
 - atomic radius
 - atomic number
 - None of these are correct.
- T/I** The condensed electron configuration for arsenic is
 - $[\text{Ar}]4s^23d^{10}4p^3$.
 - $[\text{Ar}]4s^24d^{10}4p^3$.
 - $[\text{Kr}]4s^24d^{10}4p^3$.
 - $[\text{Kr}]4s^24d^{10}4p^3$.
 - $[\text{Ar}]3s^23d^{10}4p^3$.

Use sentences and diagrams as appropriate to answer the questions below.

- T/I** Answer the following questions in your notebook.
 - What was the critical finding that suggested the atom contained a smaller particle?
 - What was the critical finding that suggested that the particle was negatively charged?
 - What was the critical finding that suggested that the same particle was found in all matter?

12. **A** Rutherford's model of the atom has been referred to as "the nuclear model," "the planetary model," and "the beehive model." What are the reasons behind each title? In your opinion, which title is the best one for Rutherford's model? Why?
13. **K/U** What is the difference between a continuous spectrum and a line spectrum?
14. **K/U** Explain how the meaning of n is similar and different in the Bohr and quantum mechanical models of the atom.
15. **A** Arrange the following in order from highest to lowest energy, and justify your answer: $n = 7$, $n = 2$, $n = 5$, $n = 4$, $n = 1$.
16. **K/U** List all of the sets of quantum numbers allowed for the first four energy levels.
17. **K/U** Explain how light and electrons each display characteristics of both particles and waves.
18. **T/I** Answer the following questions.
- Give the possible values for m_l if $n = 4$ and $l = 2$. What type of orbital is associated with these quantum numbers? How many orbitals are associated with these quantum numbers?
 - Give the possible values for m_l if $n = 3$ and $l = 1$. What type of orbital is associated with these quantum numbers? How many orbitals are associated with these quantum numbers?
 - Give the possible values for m_l if $n = 4$ and $l = 0$. What type of orbital is associated with these quantum numbers? How many orbitals are associated with these quantum numbers?
19. **C** Develop a flowchart to outline the steps of the aufbau principle.
20. **T/I** Using a basic periodic table that does not contain electron configurations, determine which element is defined by $[\text{Kr}]5s^24d^7$.
21. **T/I** The condensed electron configuration for a silicon atom is $[\text{Ne}]3s^23p^2$. Without using a periodic table, identify the group number, period number, and orbital block in the periodic table to which silicon belongs. Show your reasoning.
22. **K/U** Answer the following questions.
- What are s -block and p -block elements collectively known as?
 - What are the d -block elements known as?
 - What are the f -block elements known as?
23. **C** Using a graphic organizer such as a triple Venn diagram to record your answers, identify the models of the atoms shown below, name the scientists who developed them, and clearly indicate what the models have in common and how they differ.



24. **K/U** Explain how the first ionization energy tends to change down a group and across a period in the periodic table?
25. **A** What other properties of elements vary the same way as first ionization energy down the groups and across the periods in the periodic table?

Self-Check

If you missed question ...	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Review section(s)...	3.1	3.1	3.1	3.1	3.2	3.2	3.2	3.3	3.3	3.3	3.1	3.1	3.2	3.1	3.2	3.2	3.2	3.3	3.3	3.1	3.1	3.3	3.1	3.3	3.3